

**Studies of Lubricant Degradation, Soot Aggregation
and Soot Morphology in the Top Ring Zone of Internal
Combustion Engines**

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GLOSSARY OF TERMS

ACEA – Association Constructeur d'Europeene Automobiles
AFM – Atomic Force Microscopy
API – American Petroleum Institute
AW – Antiwear
CEC – Coordinating European Council
CRT – Cathode Ray Tube
EDX – Energy Dispersive X-ray analysis
EGR – Exhaust Gas Recirculation
EOT – End of Test
EP – Extreme Pressure
HPLC – High Pressure Liquid Chromatography
MW – Molecular Weight
PTFE - Polytetrafluoroethylene
SEM – Scanning Electron Microscopy
STM – Scanning Tunnelling Microscopy
Rpm – revolutions per minute
TBW – Through the Bore Wall
TEM – Transmission Electron Microscopy
TLC – Thin Layer Chromatography
TGA – Thermogravimmetric Analysis
TRZ – Top Ring Zone
UV - Ultraviolet
VI – Viscosity Index
VII – Viscosity Index Improver
ZnDTP – Zinc Dithiophosphate

ABSTRACT

A study was undertaken of the dispersancy characteristics of different detergent / dispersant additive packages in the piston ring zone of two operating internal combustion engines (single cylinder diesel and petrol) utilising top ring zone sampling. The dispersant type, treat level and detergent type of two succinimide dispersants at zero, half and full treat with two different detergents, a mixed salicylate type and a phenate / sulphonate type was studied. A blotter spotter method was developed by improving the method of spot size measurement by using Thin Layer Chromatography (TLC) plates and a TLC fluorescence scanner. This enabled an accurate measure of spot size expressed as a ratio of soot spot to overall oil front. It was concluded that, in the piston ring zone, dispersancy is almost independent of dispersant type and treat rate, rather the detergent package affords the dispersancy characteristics in the piston ring zone. A method for laser scattering particle size analysis was developed using a Malvern Mastersizer S to determine particle size distributions of the insolubles in the above diesel ring zone oil samples. Observations are that distinct particle size bands occur at $\sim 0.8\mu\text{m}$, $5\text{-}12\mu\text{m}$ and $>12\mu\text{m}$. In certain cases the clear particle agglomeration was observed in the ring zone over the course of the engine run where the $\sim 0.8\mu\text{m}$ size band was declining at the same time as the $5\text{-}12\mu\text{m}$ size band was increasing. Morphology studies arising from the particle size work is also covered utilising scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive x-ray analysis (EDX) techniques to show that sub-micron ($\sim 20\text{nm}$) particulates are also present with the $\sim 0.8\mu\text{m}$ particulates. The larger particles ($>12\mu\text{m}$) were also shown (by SEM/EDX) to be a distinctly different type consisting mainly of calcium, aluminium, oxygen, sulphur, magnesium and iron. These particles are most probably sulphates of calcium and magnesium with some wear particles and originate from the detergent portion of the additive pack.

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1 Background and Aims of the Investigation.

1.1 Background

1.1.1 Rationale

The drive by engine manufacturers and lubricant formulators to reduce emissions from engines has led to widespread concern for the current lack of understanding of how lubricants degrade in the piston ring zone. This has become more important as government legislation has driven down the limits of emissions from engines¹. As emissions from combustion have decreased, so the contribution from lubricants must be reduced. To comply with new regulations, emission control piston ring pack design has been developed so that there is less lubricating oil in the piston ring zone. Therefore formulated engine oil, must now perform under more severe conditions with a much thinner layer of lubricant, leading to physical and chemical breakdown of the lubricant and additive pack.

A consequence of reducing NO_x emissions from diesel engines (by the use of retarded ignition timing or exhaust gas recirculation, EGR) is the increased levels of soot in crankcase oils^{2,3,4,5,6}. This potentially unregulated growth of particulate matter has also proved detrimental to wear related problems in areas of an engine in a state of boundary lubrication, such as the valve train. Various researchers have cited particulate agglomerations as the primary factor in valve train wear and the abrasive nature of these particulates are implicated in anti-wear deterioration^{7,8,9}.

The escalating cost of running standard engine tests requires a more fundamental approach to be taken. The oxidation of lubricating oils results ultimately in the formation of carbon particulate that also consists of oil additives, which may have undergone thermal or oxidative changes and finely dispersed metallic wear particles¹⁰. The development of crankcase lubricants is performed mostly on a semi-empirical basis, due to a limited understanding of exactly how certain additives function in operation.

Evidence to suggest that detergent / dispersant additives in an engine oil were not being effective in the piston ring zone was highlighted by Jones¹¹ who observed that

the particulate size distributions, tested by laser scattering particle size analysis, of ring zone oil samples taken from an operating Caterpillar 3406B six cylinder diesel engine, showed particulate agglomerations that were much larger in size than those oil samples taken from the sump in the same test. This led to the conclusion that the detergent / dispersant additives were not performing optimally in the piston ring zone and were allowing soot, formed as a by-product of combustion in a diesel engine and swept from the bore wall to be entrained in the ring zone lubricant, to agglomerate into larger particles. The dispersant / detergent properties of the lubricant appeared to be effective in the sump oil where temperatures (~80-150°C) are much lower than the temperatures the lubricant experiences in the upper piston ring zone (~250-300°C).

The effect of these larger soot particulates in the ring zone will lead to increased wear of the bore and rings, leading to an increase in blow-by. Also, if soot is allowed to agglomerate for a length of time, it settles on the surfaces of the piston and rings to gradually reduce the effectiveness of the ring pack leading to increased emissions contribution from the lubricant. Ultimately, this results in piston rings 'sticking', increased emissions (also catalyst degradation from ash content of combusted lube oil¹²) and subsequent failure of the engine.

1.1.2 Top Ring Zone Sampling

This is a sampling technique performed by the Lubricants Research Group, under Professor Malcolm Fox, in the Department of Chemistry at De Montfort University, Leicester. The technique involves sampling lubricant from an operating engine by taking the oil directly from the piston ring zone. The philosophy of the method is that sampling the oil from the reaction zone (the area of highest temperature in an engine) will give the chemist highly degraded lubricants within ten operating hours that would take up to 250 hours in a traditional engine test for a similar level of degradation. The reason for this is that ring zone oil samples are not diluted by the sump oil.

To sample oil directly from the ring zone of an operating engine requires extensive modification of the engine to take the sampling system. The design of the sampling system is generally engine specific as each system is designed to tackle the physical

problems that arise when a sampling system is subjected to severe operating conditions within an engine. This study used a Petter AA1, air cooled single cylinder 1.86 kW diesel engine, with a flying tube top ring zone sampling system that has previously been described by Cupples^{13,14} and a Petter W1, single cylinder 2.46 kW water cooled gasoline engine, with a flying tube top ring zone sampling system that has previously been described by Thomson¹⁵.

Oil sampling using a flying tube technique involves a hole being drilled through the piston from the back of the of the top ring groove to the underside of the piston crown (Figure 1-1). A small bore steel tube, that affords some flexibility, is attached to the underside of the piston crown via a boss connected to the drilled hole in the ring groove, and this tube runs down the side of the connecting rod to an attachment at the big end.

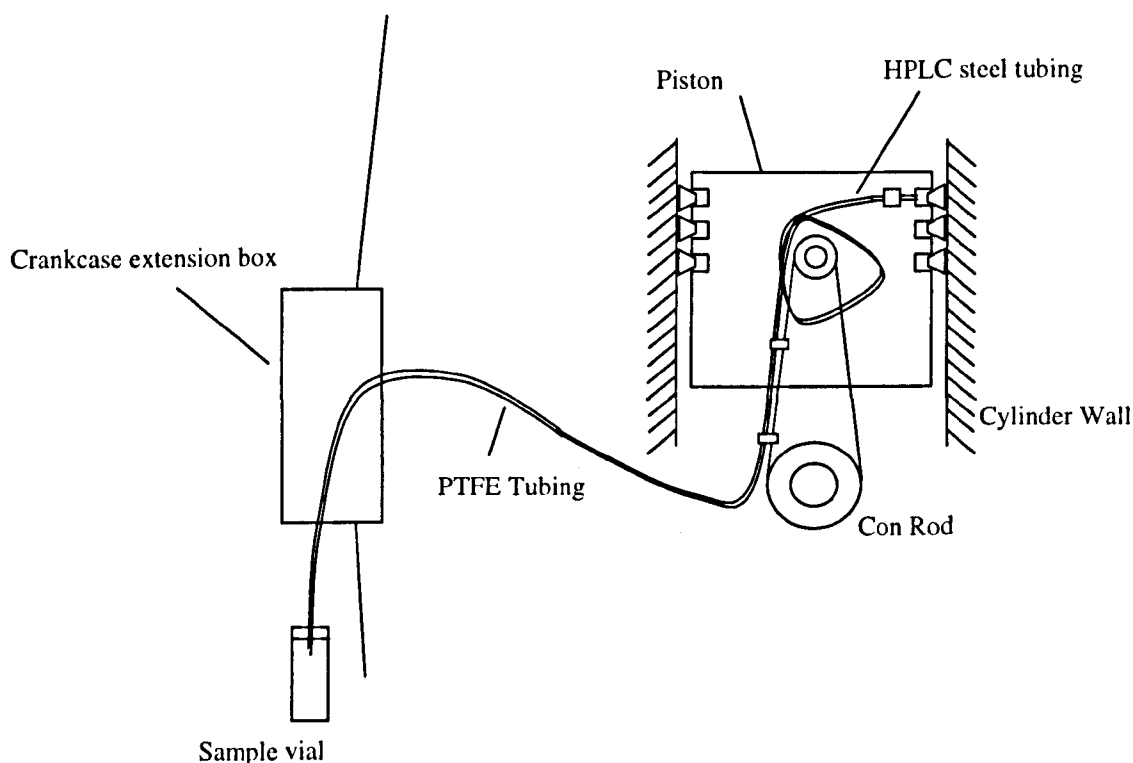


Figure 1-1 Flying Tube Top Ring Zone Sampling System

The steel tube is clamped along its length, apart from the section at the small end to allow for the relative motion between the piston and the connecting rod. A flexible PTFE tube is then connected to the steel tube at the big end. This unsupported section

of PTFE tube then loops out of the engine via a hole cut into the crankcase wall, into a crankcase extension box, which is lined with PTFE sheets, and clamped as the tube passes out of the crankcase extension box to the oil sample vial. The aim of the unsupported section of tube is to flex, such that the rotating movement of the big end versus the stationary clamp at the extension box, can be accommodated.

1.2 Oil/Additive Formulations

The study centred around two matrices of oils. The first matrix was set down in conjunction with formulators at the Castrol Technology Centre at the outset of the project. The second matrix of oil samples was formulated in response to the emerging direction the research was taking.

To control the cleanliness of the oil and piston ring / grooves in the piston ring zone, an oil formulator must pay attention to the make up of the additive package, particularly in terms of the quantity and type of dispersants and detergents used (a more in depth review of dispersant and detergent chemistry is included in chapter 2). The performance of an oil in this zone is traditionally evaluated by piston ring/ groove rating for cleanliness / detergency and by the viscosity increase of the sump oil for evaluation of the dispersancy. Currently the European ACEA Oil Sequences, which determine European oil performance levels evaluate detergency (via ring sticking and piston cleanliness) in diesel engines in the VW ICTD (CEC-L-46-T-93) or VW TDi (CEC-L-78-T-97) engine tests and dispersancy (via sump oil viscosity increase and piston cleanliness) in diesel engines in the PSA XUD11BTE (CEC-L-56-T-98) engine test.

Of particular interest in this study is the action of the dispersant in the piston ring zone. Current techniques in engine tests only evaluate dispersancy of an oil by examining the bulk sump oil viscosity. The samples are taken from sump oil at the end of test. However, the dispersant is likely to perform in a satisfactory manner in the sump due to the low temperatures involved (80-150°C). In the piston ring zone (where temperatures can be as high as 300°C) it is likely that the dispersant does not perform satisfactorily. If the dispersant is not functioning in the desired manner in the piston ring zone, then potential unregulated agglomeration of primary soot particles is possible. The function of the detergent then becomes more critical because it needs to perform some residual dispersant action and needs to work harder at keeping the piston ring and groove surfaces clean

A careful balance of dispersant and detergent types and treat rates is necessary to achieve the desired performance in the industry tests, along with satisfying the commercial and logistical interests of the oil marketer. The most common detergent types are those typified by mixed salicylate and calcium phenate / sulphonate detergent packages. The most common type of dispersant used are succinimides. The oil matrices were chosen to include these three components and to evaluate the interaction of these additives and their performance in the piston ring zone in an operating engine, through examination of piston ring zone oil samples, rather than piston ratings and sump oil viscosity. The dispersant treat rate was varied to examine confirm whether the dispersant actually performs at all in the piston ring zone.

1.2.1 First Matrix of Oils

The samples under test in this study were initially a range of related lubricants grouped into a matrix to cover differences in dispersant treat rate and using two different detergents in the additive package (Table 1-1). A full dispersant treat rate in this formulation to afford typical fully formulated oil dispersant performance is 6%. At half of this treat rate, balanced with the make up of other components in the formulation is 3.1%.

Table 1-1 First Matrix of Formulations

Formulation	Detergent	*Dispersant Treat (%)
57A	phenate / sulphonate	6
57B	phenate / sulphonate	3.1
57C	phenate / sulphonate	0
58A	mixed salicylate	6
58B	mixed salicylate	3.1
58C	mixed salicylate	0

*the dispersant is a high M.W. thermal succinimide

1.2.2 Second Matrix of Oils

After the completion of the initial results (blotter spotter test and particle size analysis) and under discussion with formulators at Castrol, it was decided that a second similar matrix of oils be formulated and tested. At this stage it was decided that the study be narrowed in it's scope to concentrate on diesel engines and so the dispersant additive was changed to a type more commonly found, and regarded by the formulators to be more effective, in diesel engine oil formulations of the time. In all of the formulations of the lubricants all other base oil, additive package components and treat rates were kept consistent. A summary of the second oil matrix is shown in Table 1-2

Table 1-2 Second Matrix of Formulations

Formulation	Detergent	*Dispersant Treat (%)
57D	phenate / sulphonate	6
57E	phenate / sulphonate	3.1
57F	phenate / sulphonate	0
58D	mixed salicylate	6
58E	mixed salicylate	3.1
58F	mixed salicylate	0

*the dispersant is a lower M.W. thermal succinimide

1.3 Experimental Testing

1.3.1 Types of Laboratory and Engine Tests

Laboratory tests can be useful in studying dispersant and detergent effects of lubricating oils. Oxidation and detergency can be studied in the laboratory using hot tube tests. This type of test flows heated oil (from a reservoir) over a hot tube (maintained at a specified temperature, using a temperature gradient across the tube or cycling the temperature of the tube) in a repeated cycle to simulate the conditions of an operating engine. Tubes of differing metallurgies can be used to simulate different engine metallurgies. The deposit on the tube at the end of test is correlated against piston merit from the engine test that the cycle was attempting to correlate too. The properties of the bulk oxidized oil are also examined and correlated. The current variant of this test, TEOST MHT-4¹⁶ is used in the American API Heavy Duty Diesel Oil categories and attempts to back correlate against the European Gasoline Engine test, the PSA TU3HT (CEC-L-55-T-95). Correlation is not wholly successful, and there is widespread concern in the industry that this test cannot adequately replace a full engine test.

Carbon black can be dosed into fresh engine oil to study dispersant effect, particularly with regards to bulk oil viscosity. Furthermore, these artificially sooted oils can then be examined in a variety of reciprocating wear tests, such as the four ball, the Cameron Plint, the pin-on-disk and others (selected according to the lubricating regime of the engine components under study). This has never been regarded as adequate as soot in a diesel engine has a different morphology to carbon black and the dispersants respond differently to this as a surrogate soot. Engine tests are preferable and the PSA XUD11BTE (CEC-L-56-T-96) remains the standard.

Complex reaction and interactions take place in an operating engine that cannot all be accounted for in laboratory tests that study specific areas and this accounts for the difficulties in correlation to known engine test performance with this type of approach.

1.3.2 Engines used in this Study

The Petter AA1 and W1 single cylinder engines were chosen for this study for a number of reasons. Firstly, top ring zone sampling has already been demonstrated and installed on these engines at De Montfort University, so development was minimal, the test cycles were already defined and the sampling system integrity was already well understood. Single cylinder engines are also logistically easier to handle in a research environment, requiring less space, less fuel, less time and cost to maintain and show little compromise versus the multi-cylinder equivalents in terms as a research tool. Single cylinder engines are much more versatile when it comes to modifications for fitting top ring zone sampling systems.

Petter AA1 Single Cylinder Diesel Engine

This engine was run under the following conditions:

- Oil Pressure – 0.2 bar
- Exhaust Temperature ~ 550°C
- Bore Temperature at Top Dead Centre ~150°C
- Sump Oil Temperature ~ 70°C
- Engine Speed – 1500rpm
- Engine Load – 24 Nm

Petter W1 Single Cylinder Gasoline Engine

This engine was run under the following conditions:

- Oil Pressure – 0.2 bar
- Exhaust Temperature ~ 550°C
- Coolant Temperature ~110°C
- Sump Oil Temperature ~ 100°C
- Engine Speed – 1500 rpm
- Engine Load – 33 Nm

1.3.3 Engine Runs

All twelve of the formulations from the two oil matrices were tested at 1500 rpm. in a Petter AA1 single cylinder diesel engine in duplicate using top ring zone sampling for a total of eight hours in each case sampling every hour. A final sump oil sample was also taken. The formulations from the initial matrix (Table 1-1) were also tested at 1500 rpm. in a Petter W1 using top ring zone sampling for a total of six hours in each case sampling every hour. A final sump oil sample was also taken. The diesel fuel used throughout was standard pump diesel (0.25% sulphur) and the gasoline fuel was standard pump unleaded. Prior to analysis, the oil samples were placed on roller apparatus for two hours to ensure sample homogeneity.

1.4 Analysis

The blotter spotter method developed and described in Chapter 3 is an investigation into remaining useful dispersancy of used top ring zone oils. Further investigations examining particle size distributions in the top ring zone oil by laser scattering particle size analysis follow in Chapter 4. Finally electron microscopy techniques in Chapter 5 were developed to examine the morphology of the particulates observed in the particle size investigations.

1.4.1 Blotter Spotter Test

This type of test is commonly used for generic analysis of remaining useful dispersancy of used oils. It is a quick and cheap field method and is unfortunately not quantitative requiring skilled judgement of the analyst to interpret the results. Samples tend to be condemned if they show only obvious signs of having very little dispersant capacity left. The test would be much more useful as an analytical technique for remaining useful dispersancy of used oils if the measurement technique can be improved upon rather than relying on the analysts eye and judgement.

For this type of test to be useful to this study of the effectiveness of dispersant / detergent types in the top ring zone of an engine then some development of this technique towards being quantitative is necessary. Chapter 3 describes the steps towards this goal, applying a fluorescence TLC scanner to the spot size measurement and improving upon the support material to silica gel TLC plates.

1.4.2 Particle Size and Aggregation Analysis

The study of the distribution of the size of soot particles from oil samples taken from the top ring zone is necessary to this study. Information on the formation of initial agglomerations of soot particles entrained in the oil in the piston ring zone and further growth to aggregations can yield information as to the effectiveness of the dispersant / detergent additive system and its performance in the piston ring zone.

One technique that can be used to study particle size distributions from powders to suspensions is laser scattering particle size analysis and this technique was developed (in Chapter 4) for the study of used oil samples. The technique has a very wide base of application and was relatively simple to turn to the study of ring zone oil samples requiring only attention to the amount of sample dosed into the system, the choice of sample receptacle in the instrument and the choice of solvent to suspend the particulate.

1.4.3 Morphology

For fundamental analysis of the type of soot, size and shape produced in the ring zone oil samples from this study, electron microscopy techniques were used. Laser scattering particle size analysis gave information on the size distributions of particulate but assumed spherical particulate in the calculations. Electron Microscopy was developed, particularly with respect to sample preparation for the study of the particles present in used oil samples. Introduction of particulate into an electron microscope is especially difficult requiring attention to be paid to the technique of separation from the oil and choice of sample support. Compositional analysis of some highlighted particulate was also undertaken utilising the electron microscope with energy dispersive x-ray analysis using image manipulation techniques to study the results

1.5 Aims and Objectives

1.5.1 Statement of Aims

The aim of the research was to determine whether detergent / dispersant additives in fully formulated engine oil were acting effectively in the ring zone of an operating internal combustion engine using top ring groove oil samples. Supporting this, development of analytical techniques to facilitate the above and development of particle sizing and electron microscopy techniques to study particulate size distributions and morphology of insolubles in the top ring groove oil samples

1.5.2 Objectives

- Use top ring zone sampling in an operating internal combustion engine on two matrices of lubricants where the lubricants differ in detergent and dispersant additive, composition and type
- Use top ring zone sampling in low speed, single cylinder petrol and diesel engines on the above formulations
- Develop Blotter Spotter technique to investigate remaining useful dispersancy of the above degraded lubricants from the top piston ring zone
- Measure particle size distribution of the above degraded lubricants from the top piston ring zone
- Microanalysis of the degraded lubricant sample by TGA and Particle Size Analysis
- Investigate the morphology of particulate from a typical top ring zone oil samples from a diesel engine using electron microscopy techniques

1.6 Layout of Thesis

This thesis continues in Chapter 2 with a review of lubrication regimes, lubrication system requirements, background on oil additives and their uses and a history of top ring zone sampling. Chapter 3 describes the Blotter Spotter Test work, Chapter 4 the Particle Size Analysis work and Chapter 5 the morphology studies using Electron Microscopy techniques. Chapter 6 reviews and concludes the work in the thesis.

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2 Historical Review.

2.1 Lubrication, Friction and Wear

2.1.1 Brief History

It was the ancient Egyptians who first discovered the use of animal fat (tallow) as a crude boundary lubricant in the axles of their carts and chariots¹. This type of lubrication, where the lubricated surfaces can still come into occasional contact, prevailed throughout the middle ages (AD450-1450) and up until the Industrial Revolution (AD1750-1850)². This brought on the invention of the steam engine and the consequent introduction of bearing surfaces in rapid relative motion. This was instrumental in stimulating a much improved and as yet unexploited technique of lubrication, in which the bearing components were no longer in occasional contact, as in boundary lubrication, but were separated by a fluid film thick enough to prevent any contact at all. To achieve this the bearing geometry was designed such that a wedge of lubricant was formed in the travelling direction of the bearing and this type of lubrication became known as hydrodynamic lubrication.

The discovery of plentiful supplies of mineral oil in the mid-nineteenth century aided this type of lubrication regime and by the end of this century the mechanisms of lubrication regimes were just about understood and expressed in mathematical terms. Since then much research has been done into understanding and improving on the various types of lubricating regimes that prevail in machinery.

2.1.2 Primary Requirements of Lubrication

It is possible for friction, and consequently wear, to be almost entirely eliminated if the moving surfaces are prevented from contact by a lubricant film. This is the basic requirement of a lubricant.

Separation of the surfaces is not the only function of a lubricant. It must also have cooling properties to reduce local heat produced from friction, must have an inherently high shear strength and must not itself contribute to any corrosive mechanisms of wear.

The necessity of fulfilling these basic requirements restricts the choice of successful lubricants to a limited number of commercially available materials of which mineral oils form by far the largest category.

2.1.3 Theory of Friction

It was Leonardo Da Vinci who developed his idea of friction into the two fundamental laws of friction:

- First Law : The frictional force is independent of the area of contact.
- Second Law : The frictional force is proportional to the load.

Friction can be defined as 'resistance to movement' and is represented in Figure 2-1.

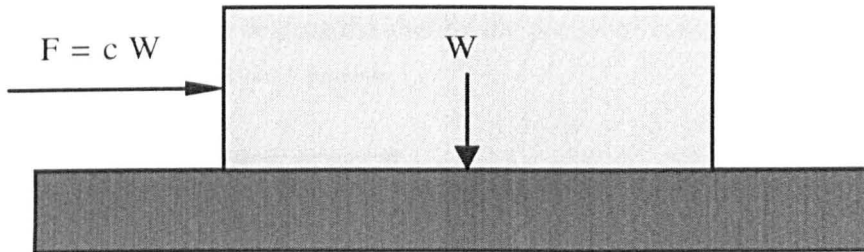


Figure 2-1 Sliding Friction.

A body of weight W rests on a surface and a certain minimum lateral force will need to be applied to the body to overcome the friction between it and the surface before sliding will occur. If F is the force required to **just balance** the resisting force of friction so that an increase would cause the body to slide then,

$$F=cW,$$

where the coefficient of friction is given by c . A lubricant reduces the coefficient of friction between the surfaces, which translates to less force needed to produce relative motion.

2.1.4 Lubrication Regimes

Optimum conditions of lubrication exist when the sliding surfaces are separated by a film of oil thick enough to prevent any metal-to-metal contact. This means that the minimum film thickness must be several times greater than the sum of the individual surface roughness measurements of the bearing components. Such films can either be maintained by an externally pressurised oil supply system, known as hydrostatic lubrication, or be self-generated by favourable surface geometry and a relative sliding velocity high enough to produce laminar flow, called hydrodynamic lubrication. The most undesirable conditions in lubrication are promoted by high loads, low speeds, extreme temperatures or lack of lubricant and these conditions lead to further classifications of the lubrication regimes, thin film lubrication and boundary lubrication. The transition from hydrodynamic lubrication through thin film to boundary lubrication is gradual and mixed states of lubrication commonly prevail.

This situation can be represented by means of the Stribeck diagram (Figure 2-2) where the coefficient of friction is plotted against the dynamic viscosity of the lubricant \times (times) the speed of the bearing divided by the pressure or loading force per unit area.

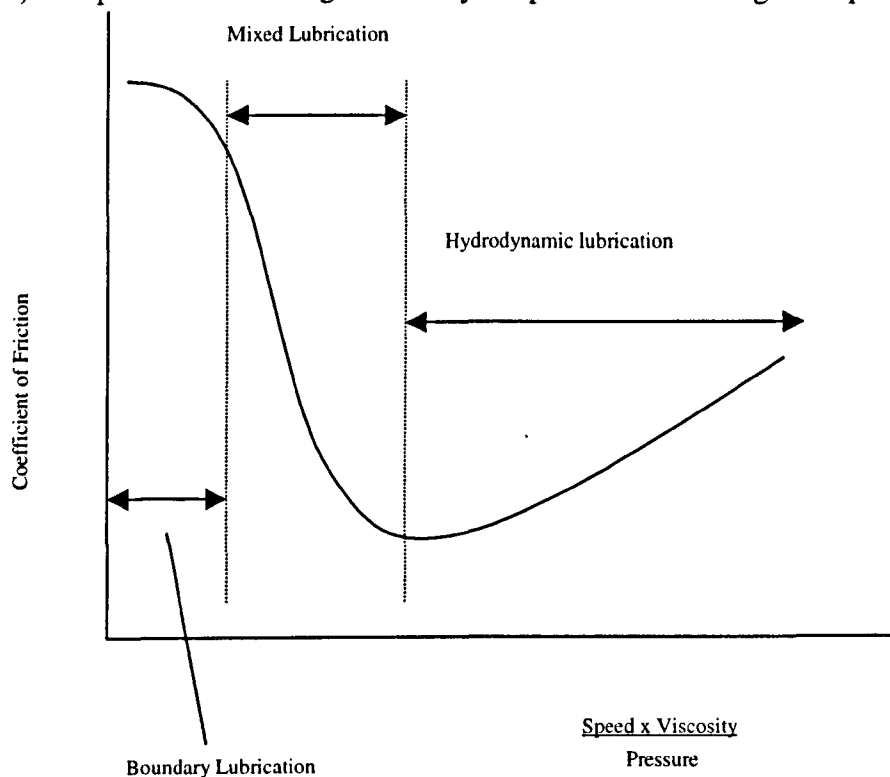


Figure 2-2 The Stribeck Diagram

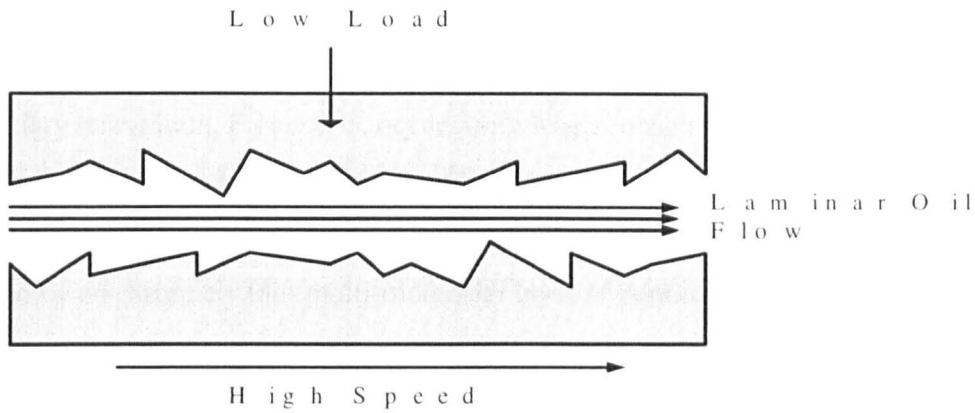
The precise shape of the curve in a Stribeck diagram would vary depending on the actual bearing design, however we can see that there is an area of minimum friction, which represents the transition between boundary lubrication through mixed states of lubrication and full fluid hydrodynamic lubrication. As lubricant viscosity and bearing speed increase, the friction rises to well above the optimum level. At low values of viscosity and speed the friction rises sharply in the area of boundary lubrication.

In an operating engine there are three principle areas associated with engine friction, the valve train, the piston ring and liner interface and the main bearings. The valve train tends to operate mainly in the boundary area of lubrication in the action of the camshafts against the cam follower. The piston ring and cylinder liner operates mostly in hydrodynamic throughout most of the engine stroke. However at the ring reversal this rapidly moves into the boundary area of friction before the piston begins to move back down the bore. The main bearings operate mostly in the area of hydrodynamic lubrication.

The oil film thickness has a direct bearing on the amount of wear that is exhibited on the surfaces. In the hydrodynamic region there is no contact between sliding surfaces and thus no wear occurs. In the boundary area of lubrication the lubricant film thickness becomes almost non-existent and so wear of the metal surface is prevalent. Each of the three areas of the Stribeck diagram are discussed below.

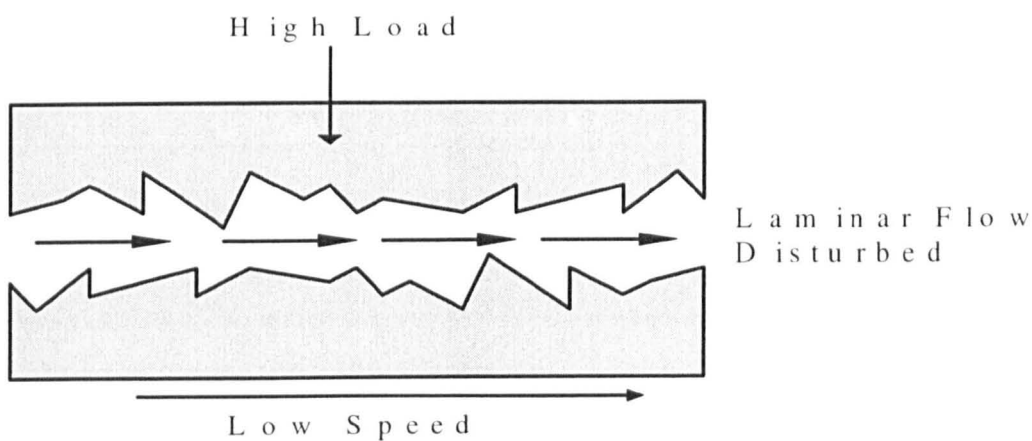
Hydrodynamic Lubrication

Having reviewed previous investigations of lubrication applications by Petrov (1883) and Towers (1885), Osbourne Reynolds^{3,4} postulated that hydrodynamic lubrication is primarily influenced by the viscous flow properties of the lubricant. The oil adheres to both the stationary and moving surfaces of the bearing and the oil is dragged into the middle so that a convergent wedge of oil is generated which builds up sufficient fluid pressure to hold the surfaces apart and carry the applied load, Figure 2-3.

Figure 2-3 Hydrodynamic Lubrication⁵.

Thin Film (or Mixed) Lubrication

In thin film lubrication, Figure 2-4, the hydrodynamic lubrication system is partially broken down due to higher loads, lower speeds, unfavourable geometry of the mating surfaces or insufficiency of lubricant, so that some lubricant is still present. Surface asperities penetrate and disturb the desirable laminar conditions of flow to that of more turbulent flow so that only part of the load is carried by hydrodynamic forces and the remainder by solid-to-solid contacts. Thin film lubrication is an intermediate state in which the laws of hydrodynamic lubrication are no longer applicable.

Figure 2-4 Thin Film Lubrication⁶.

Boundary Lubrication

Boundary lubrication, Figure 2-5, occurs only when contact pressures are high enough and sliding velocities low enough for hydrodynamic effects to be completely absent rendering the viscous properties of the oil completely ineffective. The entire load is then carried by an extremely thin multi-molecular layer of boundary lubricant. Today the term boundary lubricant is usually extended to include other types of lubricant which do not function hydrodynamically, such as chemical coatings, surface films and lamellar solids such as graphite.

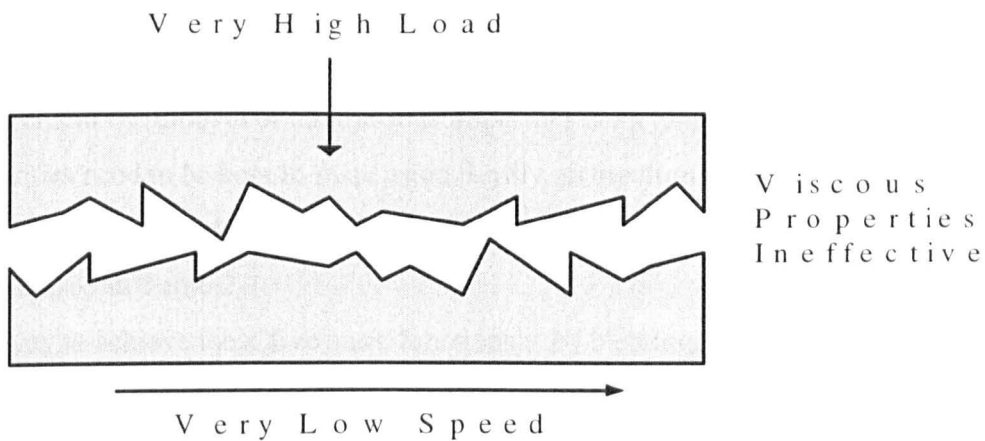


Figure 2-5 Boundary Lubrication⁷.

2.2 Automotive Crankcase Lubricants

2.2.1 The Requirements of an Engine oil

The principle function of an engine oil is that of **lubrication**^{8,9,10}, by preventing metal-to-metal contact and wear of the moving parts within an engine. Secondly, the oil must be adept at **cooling** by assisting the removal of heat from the engine mechanisms. The lower parts of the engine, such as crankcase, pistons, camshaft, timing gear etc. depend almost entirely on the oil for cooling. Thirdly, gas and oil leakage, especially in the piston ring region where blow-by of combustion gases past the piston assembly and cylinder, must be kept to a minimum, described as 'sealing'. **Cleaning** is the fourth requirement by removal of all injurious impurities from lubricated regions. These impurities need to be kept in suspension. Lastly, **protection** against chemical attack on the engine metals that are exposed to acidic products of combustion. These functions are summarised in Table 2-1.

The way to achieve these five basic functions is by blending additives into a base oil which itself is usually obtained from mineral crude oil or a synthetic replacement. These functions will be discussed under the following headings.

Oxidation Stability

The temperature of the oil and engine parts it contacts, the presence of oxygen, the nature of the metal surfaces and debris and the products of the fuel combustion, all influence the oxidation of the hydrocarbon components in lubricating oil. High temperatures are the primary factor, and the top piston ring groove and the crankcase are the critical regions. The temperature of the top ring groove can easily reach 250°C in a passenger car engine and 300°C in a heavy duty diesel engine¹¹, while in the lower parts of the engine, the bulk temperature in the sump can rise to 165°C during high speed driving. The lubricating oil when subjected to these conditions must not, through oxidation, contribute to deposit formation, even after long periods of running. These deposits would eventually lead to ring-sticking and consequently excessive blow-by due to poor sealing. The oil temperature in the crankcase is normally 120-130°C. Oil maintained at this temperature should neither form any acid products capable of

attacking the bearing alloys nor form insoluble products, which lead to deposits. Good quality mineral oils cannot withstand these temperatures, so antioxidant and anticorrosive additives are used to control these problems.

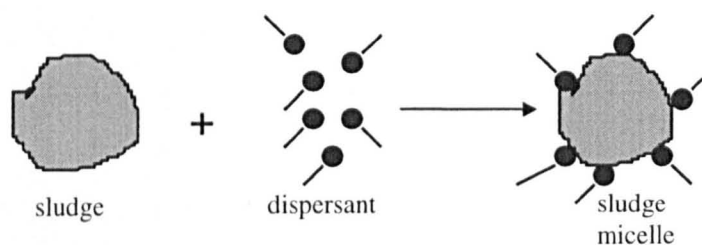
Detergency/Dispersion

Within an engine's combustion chambers the combustion process, lasting only a tiny fraction of a second, is rarely complete. Consequently, carbon and other potentially deposit forming substances are produced. These find their way into the oil lubricating the cylinder bores and are washed down into the sump. Other undesirable substances are formed when the oil reacts at high temperature with air and acidic products in combustion gases, and becomes degraded.

Detergent additives prevent deposits settling on hot surfaces such as pistons. The result of not controlling such deposits would be ring-sticking¹² (the inability of piston rings to slide sideways in their groove within the piston) disabling the rings function of pressing outward against the cylinder bore. Here, the rings are not only lubricated to prevent wear, but also to maintain a gas tight seal between the metallic sliding surfaces. The consequence of ring stick is two kinds of leakages past the rings. In one, the hot gases pass downwards from the combustion chambers to the crankcase (blow-by), further contaminating the oil. In the other, oil passes upwards and is burnt in the combustion chambers, the result is high oil consumption and more deposits. Other effects include severe wear of the cylinder bore and rings, ultimately leading to engine failure. If steps are not taken to control blow-by and oil flow, the products of combustion can intermingle with moisture and fine metallic wear particles and then agglomerate to form sludge in the cooler regions of an engine. Dispersant additives keep these solid and water droplets finely divided and suspended in the oil, Figure 2-6, and prevent both filter-blocking and the deposition of sludge. In addition, for diesel engines, the detergency helps in neutralising the acidic reaction products from the sulphur compounds in the fuel¹³.

Table 2-1 Functions and Qualities Required of Engine Oils.¹⁴

Main functions required.	Where and when.	Qualities required.
Reduce frictional resistance	During cold starting. Between con-rod/ crankshaft bearings, and journals. Between pistons, rings and cylinders.	Low enough viscosity to provide good pumping and avoid undue cranking resistance. Minimum viscosity without risk of metal-to-metal contact under the varying conditions of temperature, speed and load. Sufficiently high viscosity at high temperatures; good lubrication property outside the hydrodynamic condition, especially at top-centre. Antiseizure properties, especially during the run in period.
Protect against corrosion and wear	During shutdown or when running at low temperature. In normal running.	Must protect metallic surfaces against corrosive action of fuel decomposition products (water, SO ₂ , HBr, HCl, etc.). Must resist degradation (resist oxidation, have good thermal stability). Must counteract action of fuel and lubricant decomposition products at high temperatures, especially on non-ferrous metals. By intervention in the friction mechanism must reduce the consequences of unavoidable metal-to metal contact. Must resist deposit formations which would affect lubrication (detergency or dispersive action). Must contribute to the elimination of dust and other contaminants (dispersive action).
Assist sealing.	In the ring zone, especially at top-centre.	Must have sufficient viscosity at high temperatures and low volatility. Must limit ring and liner wear. Must not contribute to formation of deposits in ring grooves and must prevent such formation.
Contribute to cooling.	Chiefly of pistons, rings, and con-rod bearings.	Must have good thermal stability and oxidation resistance. Must have low volatility. Viscosity must not be too high.
Facilitate the elimination of undesirable products.	During oil drains to eliminate atmospheric dust, soot from diesel engines, Pb salts, wear debris, organic products from burned fuel and lubricants, and other contaminants which promote deposits or accelerate wear.	Must be able to maintain in fine suspension all solid material (dispersivity) whatever the temperature and physical and chemical conditions (water). Must be able to solubilize certain organic compounds, particularly heavy oxidation products.

**Figure 2-6 Sludge dispersion.**¹⁵

Wear Reduction

Wear is due to the individual and combined effects of corrosion, adhesion (ie. metal-to-metal contact), and abrasion. Corrosive attack by acidic products of combustion is one of the chief causes of cylinder and ring wear. Corrosive wear is effectively prevented by the use of overbased detergent additives, which neutralise the corrosive products as they form. The effect of corrosive attack is worse at low cylinder wall temperatures and so the cooling system must be designed to give more appropriate metal temperatures.

Adhesive wear affects certain parts of the engine. In the upper cylinder region, metal-to-metal contact between piston, rings and cylinder walls takes place each time the engine is started from cold due to insufficient oil in the top part of the engine. Oils with antiwear (AW) and extreme pressure (EP) additives and low viscosity at low temperatures help to provide a remedy. Adhesive wear also occurs as components such as cams (and followers), tappets, drive gears, rocker arm ends and valve stems.

Abrasion results from the presence of atmospheric dust, and metallic debris from corrosive and adhesive wear, in the lubricating oil. Efficient air filtration is therefore very important. Elimination of abrasive particle impurities from the oil system by filtration (oil filter) and periodic oil change is essential.

Viscosity

Viscosity is the most critical property of an oil. It relates directly to the oil film thickness or resistance to flow. Viscosity is directly related to how well an oil will lubricate and protect surfaces from metal-to-metal contact. Regardless of ambient or engine temperatures, an oil must flow sufficiently to ensure an adequate supply to all moving parts.

The viscosity of the selected oil must be a "tailored" or formulated compromise, partly because of the varied requirements and partly because mineral oil thins when heated and thickens when cooled. This is achieved by using additives that reduce the degree by which viscosity is affected by temperature (Viscosity Index Improvers) by endowing the lubricating oil with a higher viscosity index (VI). The VI is an empirical number indicating the effect of temperature on the changes in viscosity such that a low VI indicates a relatively large change of viscosity with temperature.

2.3 Oil Additives

The increasing level of performance demand for modern internal combustion engines has required an advance in the formulation technology of the available lubricants. As new engine designs demand even higher specification oils, then the role demanded of chemical additives increases. Modern engine oils cannot function properly without additives. The performance improvements produced by these agents are outstanding in relation to their proportion by mass, Table 2-2.

Material	% Weight
Base Oil Stock	71.5 - 96.2
Detergent	2 - 10
Dispersant	1 - 9
ZnDTP	0.5 - 3.0
Antioxidant / Wear	0.1 - 2.0
Friction Modifiers	0.1 - 3.0
Antifoam	2 - 15 ppm
Pour Point Depressant	0.1 - 1.5

Table 2-2 Composition of an Engine Oil.

These additives can be grouped into three main categories:

- those that modify the characteristics of the base oil making it more suitable for use within an engine (MODIFIERS),
- those that protect the oil to enhance it's working life (OIL PROTECTORS).
- those that protect the metallic surfaces in order to reduce corrosion, friction and wear. They enhance both the engine's working life and fuel economy (SURFACE PROTECTORS).

It is worth mentioning that some additives perform more than one role and so could fit into several of the above categories.

2.3.1 Modifiers

Viscosity Index Improvers (VII)

These additives reduce the change of the oil's viscosity with change of temperature (they raise the VI) and are the agents that enable multigrade oils to be produced. The VI-improving additives are long chain polymers / copolymers of methacrylates, olefins and alkylated styrenes. When blended with a base oil, increasing temperature causes expansion of the polymers thereby inhibiting the flow and counteracting the thinning of the oil.

Shear-stability is a primary requirement of VII's since high rubbing speeds and surface pressures between bearings in certain parts of the engine can effectively shear a 'poor' VII, rendering it ineffective.

Pour Point Depressants

Oil becomes thicker as it is cooled and the small amounts of dissolved wax left over from the refining process can crystallise at very low temperatures causing yet more thickening. The additives (polymethacrylates or alkylated naphthalenes) modify the crystalline structure in such a way as to reduce interlocking of crystals, thus enabling the lubricant to flow more easily at low temperatures. VI improvers have this function as well, as an example of multi-functionality.

Seal Swell Controllers

All engines contain gaskets and seals to prevent oil leakage at the junction of two components. Elastomeric materials of this kind must be made from rubbers that are compatible with mineral oil. Further precautions are necessary to ensure that any slight incompatibility arising from the characteristics of the base oil, or from chemical

compounds that develop during service, will not lead to shrinking and hardening of seals, either of which would allow oil to leak. The inclusion of a seal swell agent, such as an organic ester (phthalate), ensures that the oil causes very slight swelling, the best operating condition for a flexible seal.

2.3.2 Oil Protectors

Antioxidants

Oxidation of a lubricant causes the life of the oil to be reduced and this reduction is dramatic as temperature increases. An antioxidant additive slows down the oxidation process by either encouraging the decomposition of the aggressive peroxides created during the oil's normal service, or by terminating free radical reactions. Anti-oxidant materials used are zinc dithiophosphates (Figure 2-7), hindered phenols, aromatic amines and sulphurized phenols.

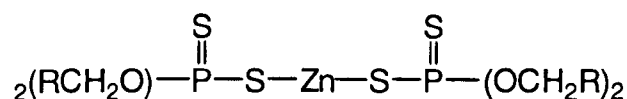


Figure 2-7 Structure of a Primary ZnDTP.¹⁶

Antifoam Agents

The crankcase of an engine could be considered as a giant egg whisk and it is easy to see why foaming can occur. Fortunately, additives such as silicones or polyacrylates minimise or prevent foaming by decreasing surface tension. Concentrations must be carefully set, as the optimum antifoam level can be critical. If foam were allowed to form then the engine would experience cooling problems, or worse still, catastrophic wear in many components by the collapse of the hydrodynamic oil film.

Metal De-Activators

Hot metallic surfaces have a catalytic effect on the oxidising influences to which oil is subjected. The oil would then deteriorate and lose its beneficial properties at an unacceptably rapid rate. The de-activators form an inert protective film on metal surfaces, thus preventing the catalytic action, and are organic compounds such as amines and phosphates, containing nitrogen, sulphur and phosphorous.

2.3.3 Surface Protectors

Antiwear (AW) Agents

In various parts of the engine, the hydrodynamic lubrication regime can break down under conditions of high load and low speed or a temporary inadequate supply of oil. Boundary lubrication arises because the physical loads exceed the load bearing capability of the oil film.

In the cam / follower (valve train) region, for example, there is a combination of heavy loading and severe wiping and the AW agents have the effect of reducing friction, preventing scoring and seizure. They undergo a chemical reaction with the metal surfaces, and create a film of solid lubricant that prevents further metal-to-metal contact. The film has a lower shear strength than metal, and its behaviour can be likened (at a microscopic level) to the soft bristles of a brush bending but not allowing contact with the backing of the brush. Agents employed for this purpose include zinc dialkyl dithiophosphates, organic phosphates and organic sulphur compounds.

Extreme Pressure (EP) Agents

EP additives are similar in purpose and function to AW additives except EP additives are expected to perform under the most severe states of boundary lubrication or even where boundary lubrication breaks down. They form compounds that will either sustain the load or shear easily and prevent welding and scuffing of the mating surfaces.

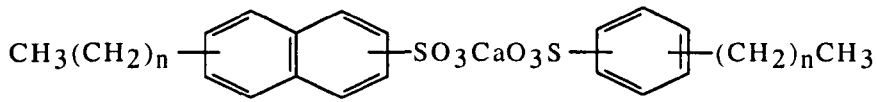
Typical materials used as EP agents are organic sulphur (such as dibenzyl disulphide), phosphorous and chlorine compounds that react with ferrous metals to form iron sulphides, phosphides and chlorides.

Corrosion Inhibitors

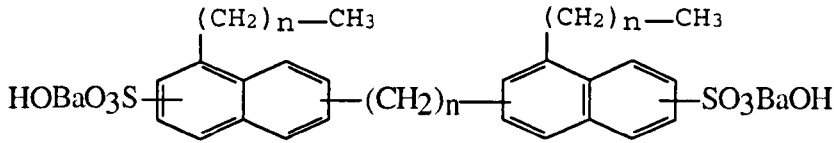
Corrosion in an engine can be regarded as being far more serious problem than the vehicle itself rusting. However, the problem, which manifests itself either due to water condensation, particularly when the engine is stopped, or due to acids formed from oxidation, is normally curtailed with the inclusion in the formulation of detergency and antioxidant additives. Corrosion additives work by emulsifying small droplets of water, neutralising acids, and by forming a protective film on metallic surfaces. The agents used include zinc dithiophosphates, metal sulphonates, fatty acids and amines. Again, various compounds from previously described properties can be effective due to their multiple functions.

Detergent/Dispersant Additives

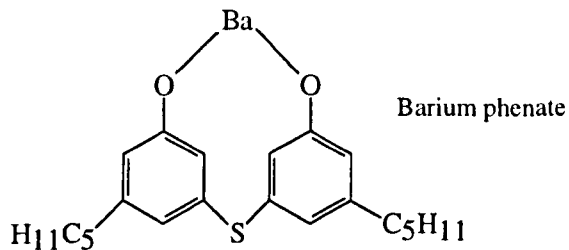
The function of these additives are to keep soot, gums and oil oxidation products finely dispersed in suspension, otherwise they would coat metal surfaces causing varnishing or lacquers or settle out as sludge in the oilways and the sump. The detergency agents are organo-metallic compounds such as calcium, magnesium or barium phenates, sulphonates or salicylates, Figure 2-8 . Most detergents employ an excess of metal to increase basicity and aid the neutralisation of harmful acidic by-products of combustion. This type are referred to as 'over-based' detergents.



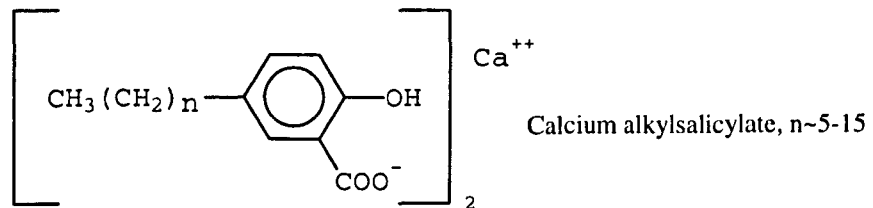
Calcium petroleum sulphonate n~20



Basic barium sulphonate, n~20



Barium phenate



Calcium alkylsalicylate, n~5-15

Figure 2-8 Some typical molecular formulae of detergent additives.¹⁷

Figure 2-9 shows a stylized detergent. A detergent works by adsorption to form a non-adhesive surface film on the metal and by coating the contaminating particles, to make them non-adhesive. The detergent additives are mainly included to handle high temperature deposits such as lacquers on the pistons and carbonaceous deposits in the piston ring area, particularly encountered in diesel engines.



Figure 2-9 Stylized Detergent Polar Substrate.

Non-metallic (ashless) dispersant additives (polyesters and alkylsuccinimides), Figure 2-10, are used to suspend oil-insoluble resinous oxidation products and particulate contaminants in the bulk oil¹⁸. They function by surrounding the minute particles of contaminating matter with a molecular coating, so that they remain in suspension rather than agglomerate to form sludge, especially at low temperatures, which is particularly related to abrasive wear and viscosity increase.

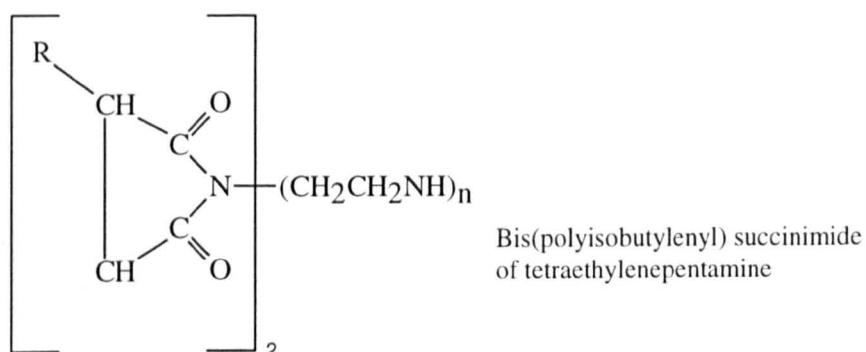
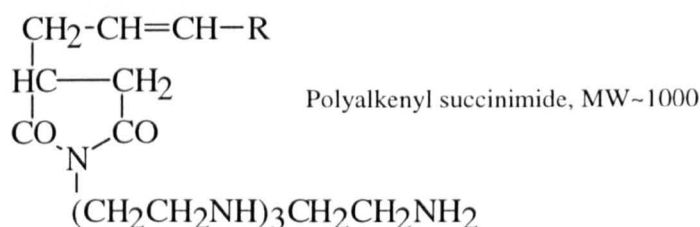


Figure 2-10 Examples of molecular formula of some dispersant additives.¹⁹

A dispersant molecule contains an oleophilic hydrocarbon moiety and a polar functional group, Figure 2-11. The polar group, usually oxygen- or nitrogen-based, attaches itself to the oxidation products and sludge particles, while the oleophilic hydrocarbon ‘tail’ keeps the particles suspended within the oil. The hydrocarbon radical is either oligomeric or polymeric, and is usually aliphatic in nature. It contains from 70 to 200 or more carbon atoms to ensure good oil solubility, with a polybutenyl alkyl group being the most commonly used hydrocarbon group. Sometimes, the hydrocarbon moiety is derived from high molecular weight polymer, such as olefin copolymer, polyacrylate, or styrene-ester copolymer.

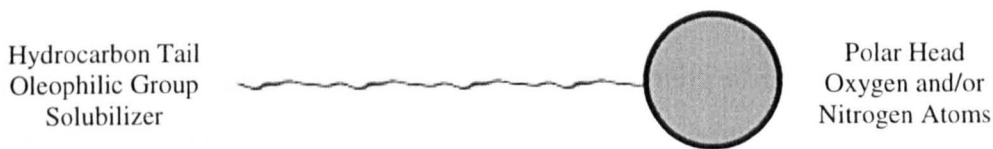


Figure 2-11 Stylized Dispersant.

2.4 Lubricant Sampling

The major wearing components of an engine are bearings, pistons, piston rings, cylinder bore and components in the valve train. The lubricant condition is a significant factor in the mechanisms of wear in these areas. One area of particular interest is that of the piston ring zone. Lubricant in this zone is highly degraded, as it is so close to the reaction zone of the engine i.e. the area of the engine under the greatest pressures, temperatures and the area where combustion and chemical interactions take place. From this it leads that it is desirable to extract lubricant from the piston ring zone, while the engine is operating, to study the lubricant condition in this zone.

Traditional oil sampling has centred on sump sampling where the highly degraded oil from the reaction zone has become diluted into the sump oil. Many hours of engine running are necessary to obtain lubricant that is degraded enough for useful analysis. Various researchers have devised methods to obtain the piston ring zone oil while the engine is running. These methods can be described as Through the Bore Wall Sampling (TBW) and Top Ring Zone Sampling (TRZ)

2.4.1 Sump Sampling

Lubricant sampling from an operating engine under laboratory test conditions is traditionally achieved by taking oil samples from the sump oil during set periods in the test. This type of engine testing can typically require 250 hours of engine running to achieve the required and measurable changes in the lubricant properties, which are pertinent to the test. Such property changes include physical and chemical changes in the lubricant. Once the sample is obtained then property changes of the oil can be investigated by a whole range of analytical tests. Viscosity techniques, infra red, thermogravimetric techniques, microscopy techniques, particle analyses and separations techniques are just a few of the available analyses.

2.4.2 Through the Bore Wall Sampling (TBW)

Dimitroff^{20,21} used a slot on the piston/port in the cylinder wall to sample lubricant from the bore wall adjacent to the piston ring zone. The system also sampled blow-by gases and as such was less suited to lubricant sampling due to lack of sealing with inherent ingress of sump oil during the non-pressurized stroke.

Baker et al²² used a capillary passage in the cylinder wall adjacent to top dead center (TDC) to transport bore wall oil and gas outside the engine which demonstrated that there was a standing ring of lubricant in a state of dynamic equilibrium in the upper piston ring zone. The method provided samples that had been subjected to the conditions of the piston ring zone.

Richard²³ also used this technique by drilling a 1mm orifice in the bore of a Petter AVB and Caterpillar 1G2 that bisected the upper piston ring zone, while Bush²⁴ used the system on a natural gas fuelled Villiers engine. Finally Cupples²⁵ using a condenser in the sampling line to improve sample yield, used the system on a Petter AA1 for comparison to previous workers results.

Ultimately TBW sampling has been found to be of limited value in comparison to TRZ sampling due to the extreme conditions the TBW samples are subjected too, preferring the slightly less degraded lubricant found in the ring pack.

2.4.3 Top Ring Zone Sampling (TRZ)

The technique involves sampling lubricant from an operating engine by taking the oil directly from the piston ring zone. The philosophy of the method is that sampling the oil from the reaction zone (the area of highest temperature in an engine) will give the chemist highly degraded lubricants within ten operating hours that would take up to 250 hours in a traditional engine test for a similar level of degradation. The reason for this is that ring zone oil samples are not diluted by the sump oil.

An early version of TRZ sampling was used by Quillan²⁶, who used a trombone type arrangement. One tube was attached to the piston and the other tube attached to the main bearing housing, with one tube sliding in and out of the other to divert blow-by gases, collecting them outside of the engine. The system also trapped oil from the appropriate region of the engine, though this was not the subject of analysis.

Further TRZ sampling techniques have been developed in the Lubricants Research Group, under Professor Malcolm Fox, in the Department of Chemistry at De Montfort University, Leicester (formerly Leicester Polytechnic). To sample oil directly from the ring zone of an operating engine requires extensive modification of the engine to take the sampling system. The design of the sampling system is generally engine specific as each system is designed to tackle the physical problems that arise when a sampling system is subjected to severe operating conditions within an engine. This project used a Petter AA1, single cylinder diesel engine, with a flying tube top ring zone sampling system that has previously been described by Cupples^{27,28} and a Petter W1, single cylinder gasoline engine, with a flying tube top ring zone sampling system that has previously been described by Thomson²⁹. Other flying tube sampling systems have been applied to the Caterpillar 1Y73 and the Villiers C30 by Cupples and Seare³⁰ respectively.

The TRZ system works by utilising the pressure difference between the combustion chamber / ring pack during the power and compression strokes, and the atmospheric pressure in the collection vessel, to drive the oil sample through the system. The oil that is collected can then be tested for degradation . Cupples also used the system to sample oils from the upper face of the Petter AA1 and Petter AVB, comparing the results to those of samples from the sump, TBW and TRZ.

The original flying tube sampling systems lasted approximately 20 hours, and as applied to the Petter AA1 by Cupples, was used to sample from various points on the piston. Only one position was used at a time to avoid oil starvation issues. In general the system followed that described in section 1.1.2 with the following points of note:

- A nylon guard tube was used to protect the PTFE tubing down the length of the conrod.

- The crankcase extension box used PTFE plates to protect the flying tube from premature wear.
- A PTFE coating was applied to the crank webs to further improve system life.

The main issues encountered in the development of the system centred around the lateral motion of the tube, which led to abrasion of the tube on all adjacent surfaces, ultimately resulting in system failure but no effective solution was found to counteract the lateral motion issue. Cupples went on to develop the system on a Caterpillar 1Y73 (which permitted upper face and top ring groove samples) and improved system life to around 50 hours with the following point of note:

- Optimised the departure point from the big end achieved by strengthening the boss on the big end by utilising Swagelock fittings with a length of steel tube.
- Thicker wall tube was also tried to minimise the lateral motion but failed due to fatigue.

Again the majority of system failures resulted from the abrasion of the tube due to lateral motion with no real effective solution being found.

Thomson applied the Petter AA1 system to the Petter W1. The main advantages to the system as applied to the W1 were that the system was aided by lower engine speed and hence tube motion. Also failures due to soot blocking the sampling tube were now eliminated, as the W1 is a gasoline engine while the AA1 is a diesel engine. Main points of note were:

- Samples were taken from the thrust side of the piston, while the system exited on the carburettor side.
- The system comprised 1/16" ID PTFE tube and 0.003" ID HPLC steel tubing.
- PTFE coating was again used on the webs of the crank.
- A guard tube was used down the length of the con rod, initially copper but later nylon held with small aluminium brackets.
- PTFE plates again used in the crankcase extension box.

Again the system failures due to the lateral motion of the tube were never solved.

Seare used various modelling techniques to fully develop a system. The first were modelled on a rig then transferred to a motored engine. On the rig, strobe lighting was

used to measure the tube motion / stability, the aim being to find out when or why the tube motion became out of control. He also conducted the first significant investigation into the lateral motion of the tube, and noted that it was very sensitive to both tube length and engine speed., resulting in the tube being briefly supported by the crank webs at certain points during the engines revolution and whipping violently at the extremes of motion. From this modelling work, primarily on the Villiers C30, Seare concluded the following:

- The sample tube must not be excessively long as it otherwise leaves the tube more susceptible to lateral motion. A shorter tube is generally more stable but gives greater stress concentrations during stable motion.
- Bringing the engine up to speed quickly did not make a significant improvement on stability.
- Angles of the take off points were too severe leading to high stress concentrations. The modelling allowed optimisation of this parameter.
- The natural set of the PTFE tube from when it is coiled on a drum immediately after manufacture caused instability problems. Seare attempted to remove this by straightening the tube with weights prior to testing. Later researchers utilised this natural bend of the tube by just orienting the tube in the system favourably.

Taking the lessons learned from the modelling, the Villiers C30 was then motored for an extended period (1500rpm, 36 hours). The tube was then inspected and showed only minor abrasion, but no imminent failure. The AA1 system was then redeveloped taking the lessons learned from the modelling exercise with the following points of note:

- No guard tube was fitted
- The piston skirt loop was fitted for the first time. This is where the upper sampling tube (from the sampling hole in the ring groove to the boss on the base of the con rod) is looped over the small end allowing flexible motion of the upper tube.
- PTFE guide plates again fitted in the crankcase extension box.

- Tube tightened / shortened slightly once the engine had reached operating temperature to compensate for both the extension of the tube due to higher temperatures and the tube stretch due to the stresses produced.

By using these procedures the sampling system passed a 20 hour test without significant abrasion. In the project described in this thesis, this same system was able to stay intact for in excess of 200 hours. This was achieved by very careful attention to the points above in the installation of the system.

Seare then paid attention to the system on a Caterpillar 3406B. The sampling system was successfully modelled on the rig, the main points of this system being:

- Shrink-wrap nylon tube was used to guard and locally stiffen the PTFE tube. Due to the significantly longer stroke of the engine compared to previous engines, the tube was necessarily longer than those used before and was very sensitive to lateral motion. The guard tube did not significantly improve the system stability.
- HPLC steel tubing was used through the bulkhead joints in the system to prevent crushing from the clamps.
- Tube tightening again used after the engine had reached operating temperature
- Reliability came to the system mainly from attention to detail in setting up the system.

Subsequently Jones³¹ developed the system on the Caterpillar 3406B. Instead of a flexible section of PTFE tube between big end and crankcase extension box, a linkage is mounted from the base of the piston skirt to carry the flexible tube (inside a rod fixed to a swivel joint), to a point outside the crankcase. This meant that the lateral motion issue couldn't occur which significantly improved system life. The sealed swivel joint allowed the sample to pass from the HPLC/PTFE used in the piston skirt, eliminating the whole of the con rod mountings. This type of system became possible due to the size of the piston being much larger than any that had had TRZ sampling systems applied before (and unfortunately can only be fitted to large engines). The two other primary factors, which made the system inherently more reliable, were:

- Lower relative motion. The velocity and displacement otherwise needed to be absorbed by the tube were reduced
- No surface for the tube to abrade against leaving fatigue as the only issue. In practice fatigue was rarely significant.

¹ BP Trading Ltd, *Lubrication Theory and it's Applications*, BP Trading Ltd, London, 1969, Ch.1, p3.

² Dowson, D. *History of Tribology*, Longman Group Limited, London, 1979, pp1-677.

³ BP Trading Ltd, *Lubrication Theory and it's Applications*, BP Trading Ltd, London, 1969, Ch.6, pp43-47.

⁴ Reynolds, O. On the theory of lubrication and it's application to Mr Beauchamp Tower's experiments, including an experimental determination of the viscosity of olive oil. *Phil. Trans. R. Soc.* **177**, pp157-234.

⁵ BP Trading Ltd, *Lubrication Theory and it's Applications*, BP Trading Ltd, London, 1969, Ch5, p38.

⁶ Ibid, Reference 5.

⁷ Ibid, Reference 5.

⁸ Rizvi, Q., *Lubricant Additives and their Functions*, The Lubrizol Corporation.

⁹ Sietoff, F. X. and Musser, J. L., What does the Engine Designer Need to know about Engine Oils ?, *SAE 821571*, 1982.

¹⁰ Pears, R., What is in your Engine Oil?, *Mining Technology*, November 1987.

¹¹ Mortier, R. and Orszulik, S. T. (Eds.), *Chemistry and Technology of Lubricants*, Chapman and Hall, London, 1994, p114.

¹² Mortier, R. and Orszulik, S. T. (Eds.), *Chemistry and Technology of Lubricants*, Chapman and Hall, London, 1994, pp62-64.

¹³ Ibid, Reference 12.

¹⁴ Schilling, A. *Motor Oils and Engine Lubrication*, Scientific Publications, 1968.

¹⁵ Mortier, R. and Orszulik, S. T. (Eds.), *Chemistry and Technology of Lubricants*, Chapman and Hall, London, 1994, p73.

¹⁶ Mortier, R. and Orszulik, S. T. (Eds.), *Chemistry and Technology of Lubricants*, Chapman and Hall, London, 1994, p105.

¹⁷ Fox, M. F., Pawlak, Z. and Picken D. J., Inverse micelles and solubilization of proton donors in hydrocarbon formulations, *Trib. Int.*, **24**, No.6, December 1991, pp341-349.

¹⁸ Ibid, Reference 8.

¹⁹ Ibid, Reference 17.

²⁰ Dimitroff, E. et al Low Temperature Engine Sludge – What? – Where? – How? *SAE 650255*

²¹ Dimitroff, E. et al Why, What and How: Engine Varnish, *Journal of Lubrication Technology, Transactions of the ASME*, July 1969 pp406-416

²² Baker A., et al Dynamic Operating Factors in Piston Rings, *ImechE 1973 International Symposium of Marine Engineers*, Paper 256 2.5.59 – 2.5.70

²³ Richard, G. P. Lubricant Properties in the Diesel Engine Piston Ring Zone, *Proceedings 8th Leeds-Lyon Symposium on Tribology*, Paper VII(I), 1982, pp 171-175

²⁴ Bush, G. B. An Investigation into Piston Ring Blowby and its effects upon Biogas Engines, PhD Thesis, Leicester Polytechnic 1986

²⁵ Cupples S. D., *Lubricant Condition in the Upper Piston Ring Zone of Single Cylinder Diesel Engines Under Operating Conditions*, PhD Thesis, De Montfort University, 1992.

²⁶ Quillan R. D., et al, Cleaner Crankcases with Blowby Diversion, *SAE January 1964* Republished in *SAE Progress in technology handbook Vol 12*, 1968, pp429-433

²⁷ Cupples S. D., *Lubricant Condition in the Upper Piston Ring Zone of Single Cylinder Diesel Engines Under Operating Conditions*, PhD Thesis, De Montfort University, 1992.

²⁸ Cupples, S. D., et al, A Study of Lubricant Condition in the Piston Ring Zone of Single Cylinder Engines Under Typical Operating Conditions, *SAE 881586*.

²⁹ Thomson, A. L., *An Accelerated Method to Assess Lubricant Degradation in the Piston Ring Zone of Spark Ignition Engines*, PhD Thesis, De Montfort University, 1995.

³⁰ Scare K. D. R., Accelerated Methods for Determining Oil Deterioration in an Internal Combustion Engine, PhD Thesis, De Montfort University, 1994

³¹ Fox M. F., Jones C. J., Picken D. J., Kelley F. A., Degradation of Lubricants in the Piston Ring Zone of Operating Internal Combustion Engines, *Condition Monitoring 1994*, Univ. Wales 21-25 March 1994, Pineridge Press, Ed Jones MH, pp470-480

3 Blotter Spotter Test.

3.1 Theory and Methodology

3.1.1 Theory of The Blotter Spotter Test

Dispersant additives function by keeping the minute particles of contaminating matter in suspension within the oil rather than allowing them to agglomerate to form sludge and deposits. Any analytical technique that can measure the effectiveness of a dispersant, must distinguish between free and bound additive.



The classic blotter spotter test¹ is not a quantitative analysis of remaining useful dispersancy. A small spot of soot laden used oil is applied to a piece of filter paper, laid flat and allowed to spread through the paper. Over time this produces a distinct series of rings. An oil that has little remaining useful dispersancy will tend to show a tight black spot of soot whereas the soot would be carried a certain distance (shown as a ring front) if the dispersant was still functioning to some degree. The test, as it stands, can only give general indications of remaining useful dispersancy between similar samples or samples of the same series.

The advantage the blotter spotter test retains is that the oil sample can be analysed as it is without any interactions or interferences from solvents that can upset the balance of the equilibrium between free and bound dispersant. Many other analytical techniques do introduce a solvent at some stage, and in effect, are then only a measure of insolubles levels in the sample.

3.1.2 Improving upon the Blotter Spotter Test

The Blotter Spotter Test is somewhat limited in scope as the accuracy of this type of method can depend upon the type of blotter paper used, the operator and especially when interpreting the results, the operators skill and judgement. There is currently no measurement technique for the oil spots produced.

A more consistent support for the oil spots can be found in silica gel TLC (thin layer chromatography) plates. These can then be used in a TLC scanner to gain accurate measures of the spot and oil front sizes.

The soot ring front produced could be measured relative to the final oil front. This oil front is usually difficult to see accurately with the naked eye. To get a measure of the relative soot and oil fronts a TLC densitometer (Camag TLC Scanner 3) was used at a wavelength of 366nm. 254nm was also available but it was found that the plates themselves fluoresced at this wavelength. 366nm was chosen because the base oil fluoresces at this wavelength. The densitometer scans a slice of the spot across the diameter taking a data point every 25µm at a scanning speed of 10mm per second. The instrument measures the reflection intensity from the plate. This gives a fluorescence spectrum across the spot. The soot ring would give little reflection while the oil front would be expected to fluoresce significantly. Examples of oil spots under visible light and UV light at 366nm are showed in Figure 3-1 and Figure 3-2 respectively.

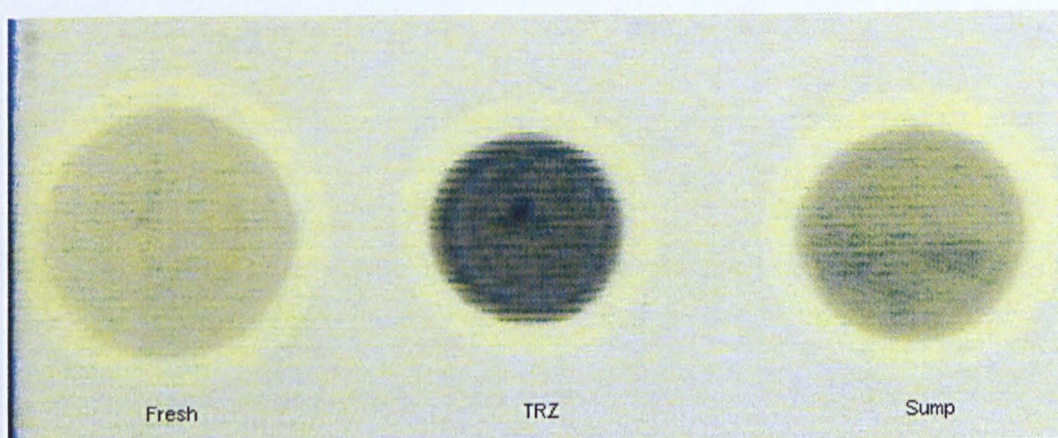


Figure 3-1 Examples of Spots of Fresh, Top Ring Zone and Sump Oils



Figure 3-2 Examples of Spots of Fresh, Top Ring Zone and Sump Oils Under UV Light (366nm)

A representation of a typical TLC scanner plot is shown in Figure 3-3. A ratio of the total oil front versus the soot spot front can be a measure of the effectiveness of the dispersant. D_f denotes the diameter of the oil front while D_b denotes the diameter of the soot spot. D_b is measured between the two least reflective parts of the spectrum, which correspond to the limit of the soot front. As a quick check these values can be compared to the straight TLC plates to ensure the correct fronts are being measured.

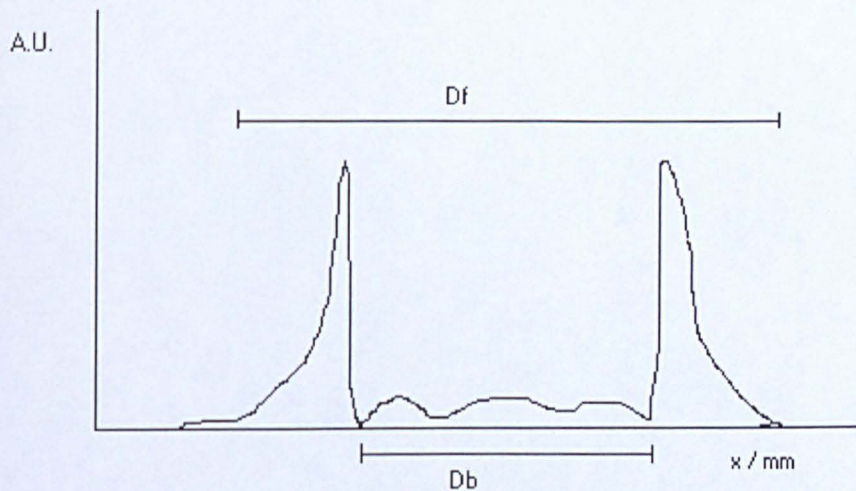


Figure 3-3 Representation of Typical TLC Scan

The spot ratio can be gathered for a series of oils to track the effectiveness of the dispersant, for example, in the top ring zone versus engine run time. A good spot ratio is one where the oil has carried the oil front far (a large ratio) and a bad spot ratio can

be regarded as one where the particulate front has not been carried very far at all by the oil (small ratio).

The technique introduces some accuracy into the spot measurements and allows a correction for the amount of oil applied as a spot. It is difficult to apply a spot with the same liquid volume and pressure. Specialised spotter equipment is available for this but was not available. This would improve the technique further.

3.2 Results

The samples examined were from the first matrix of oil samples that had been run in the single cylinder diesel and petrol engines, as previously described. The formulation data for the oil samples is shown in Table 1-1.

Each of the oil samples were analysed by the blotter spotter / TLC scanner method described in the previous section. For the gasoline engine oil samples, there are no results for the end of test sump sample as there was just too little particulate to form a coherent and measurable ring front.

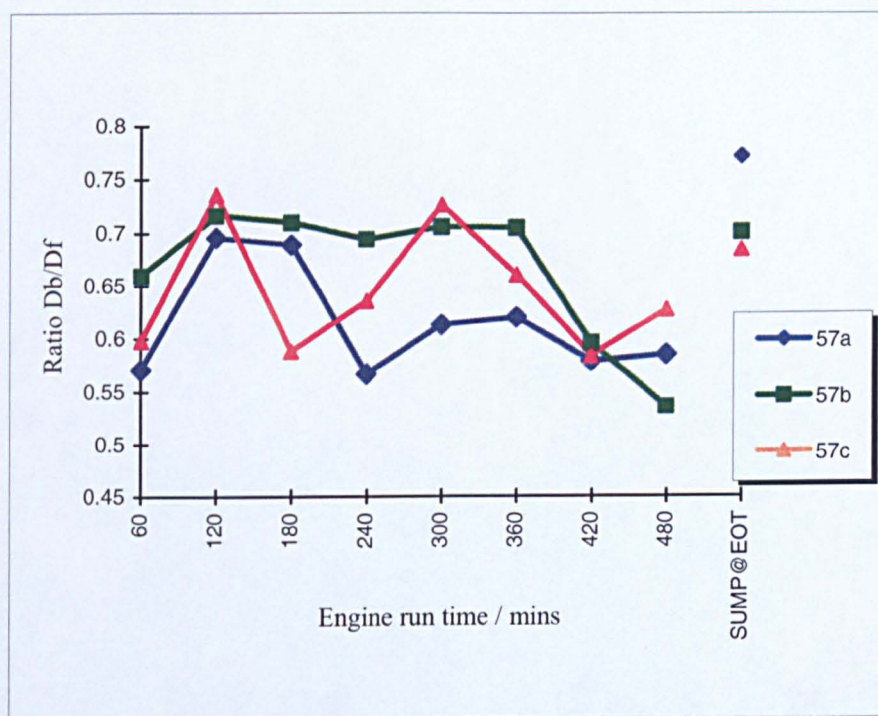


Figure 3-4 Particulate Ring Ratio vs Time of 57a/b/c Series Oils from the AA1 Diesel Engine

The results for 57a/b/c in the diesel engine are shown in Figure 3-4. The detergent in this series is a phenate/sulphonate while the dispersant is a succinimide type. The detergent / dispersant package in this series is very erratic in the TRZ in terms of dispersancy performance through the course of the engine run. The half treat dispersant oil (57b) performs well in the TRZ until 360 minutes where the dispersancy of the oil in the TRZ drops off suddenly. The end of test sump sample is

at approximately the same level as the samples from the first 360 minutes. The full dispersant treat version (57a) performs poorly throughout the whole test but shows the best performance in the end of test sump sample. The zero treat dispersant oil (57c) that is relying solely on any dispersant effect the detergent package might afford, is unpredictable. With no dispersant, any soot would not disperse properly in the oil, especially in the ring zone and so this is expected. The end of test sump sample does fall below the half treat oil, placing it in the expected sump sample ranking. It seems overall that this detergent / dispersant package performs poorly in the top ring zone but performs as expected in the sump.

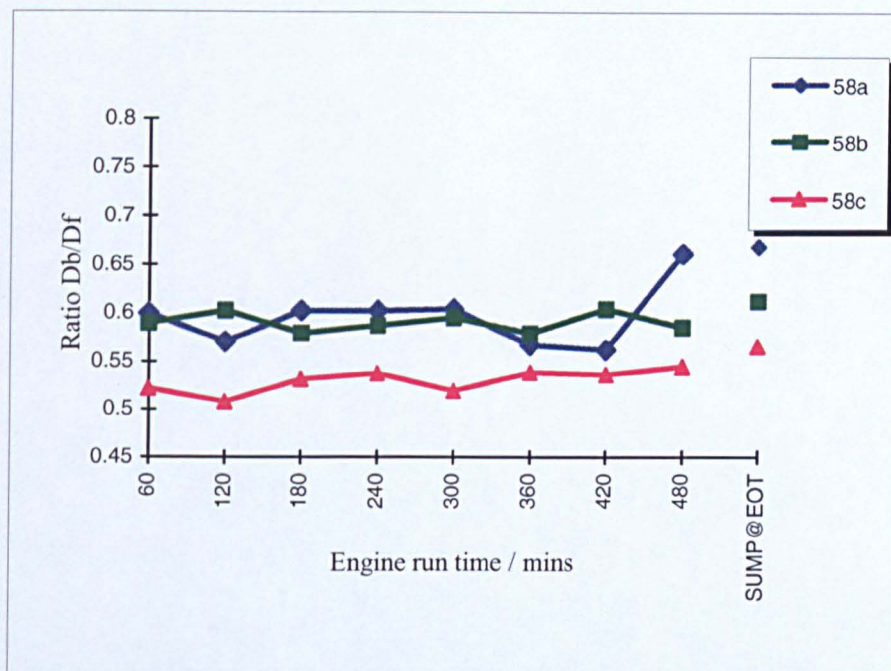


Figure 3-5 Particulate Ring Ratio vs Time of 58a/b/c Series Oils from the AA1 Diesel Engine

The results for 58a/b/c in the diesel engine are shown in Figure 3-5. This series has a different detergent package and performs more consistently in the top ring zone than the 57 series oil. The sump samples are clearly discriminated and the half treat dispersant oil is very consistent. The full treat oil is more erratic but is generally better than the half treat oil. The only difference between the 57 and 58 series oils is the change from a phenate/sulphonate to a mixed salicylate detergent pack. Therefore any improvements in dispersancy performance can only be due to the salicylate detergent. The inference is that the mixed salicylate detergent is more effective in its role as a 'secondary' dispersant than the phenate / sulphonate detergent in the 57 series oils. There also seems little advantage (in the ring zone) of 6% dispersant treat vs 3%

dispersant treat in either the 57 or 58 series oils. However, the advantage of the higher treat rate is clear in the sump oil. The dispersant is performing poorly in the ring zone, but is performing well in the sump.

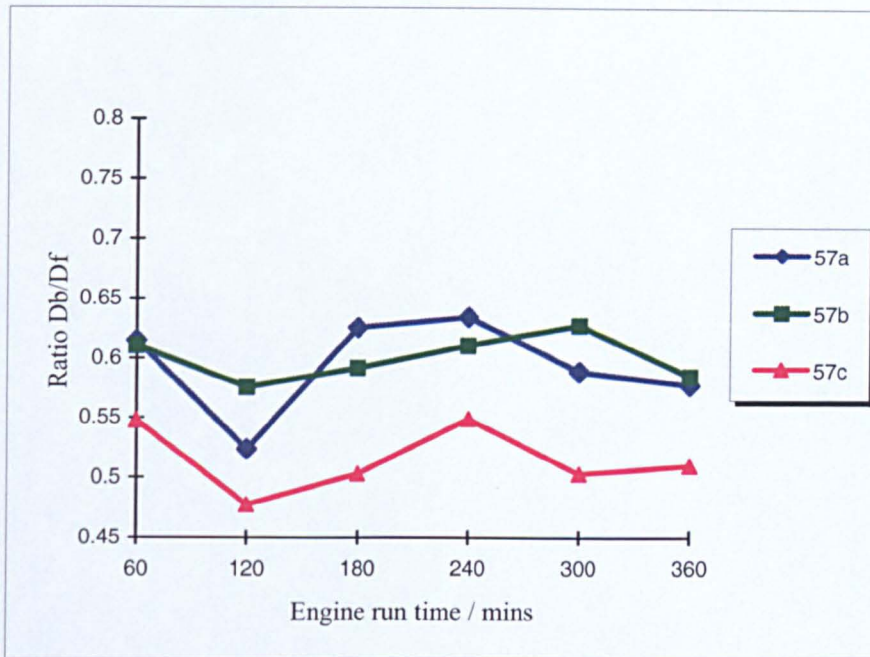


Figure 3-6 Particulate Ring Ratio vs Time of 57a/b/c Series Oils from the W1 Gasoline Engine

The results for 57a/b/c in the gasoline engine are shown in Figure 3-6. The gasoline engine produces less particulate than the diesel engine and so the dispersant might be expected to have performed better than in the diesel engine, and indeed this is the case. The results are quite consistent for the zero treat dispersant oil (57c) again suggesting the detergent is performing to some extent as a dispersant. The half treat dispersant oil (57b) is also relatively consistent but performing better than 57c. This was not the case in the diesel engine, which suggests that the dispersant performs better in the gasoline engine. There is no improvement, however, in the full treat dispersant oil (57a) over the half treat dispersant oil. In fact 57a is less consistent than 57b in the gasoline engine.

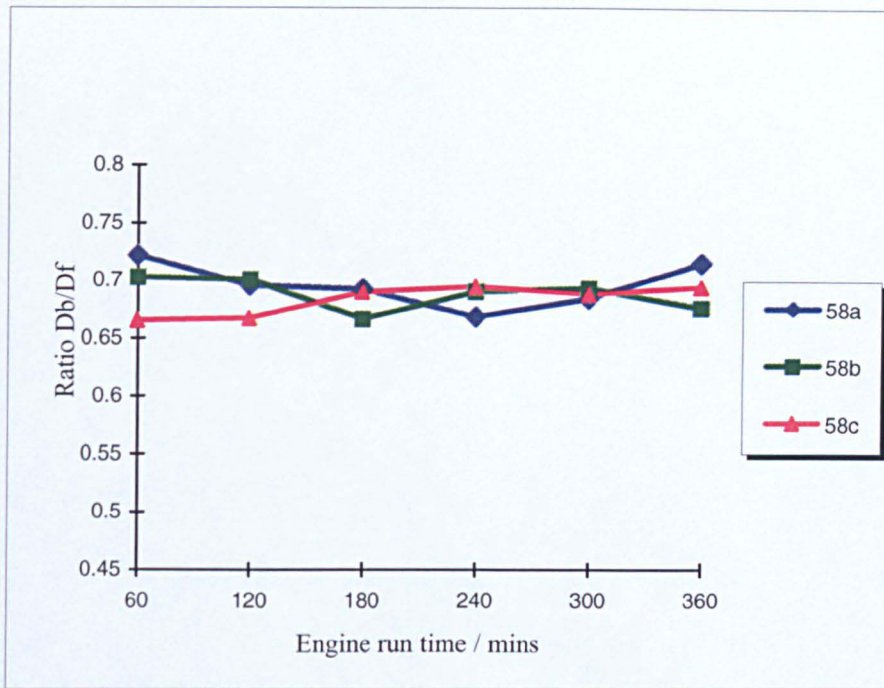


Figure 3-7 Particulate Ring Ratio vs Time of 58a/b/c Series Oils from the W1 Gasoline Engine

The results for 58a/b/c in the gasoline engine are shown in Figure 3-7. All of the results for this series in the gasoline engine are roughly equal. The dispersancy performance of these oils in the top ring zone seems independent of the dispersant treat rate. Of both 57 and 58 series of oils, this combination of succinimide dispersant and salicylate detergent in the gasoline engine yields the best results in terms of top ring zone dispersancy performance.

From the results of these oil series, the inference is that the salicylate detergent pack in conjunction with the succinimide dispersant is acting with superior dispersancy characteristics than the phenate / sulphonate detergent pack in conjunction with the succinimide dispersant in the top ring zone.

3.3 Discussion

The succinimide dispersant used in the 57a/b/c and 58a/b/c oil series does not appear to be successful in the top piston ring zone. The high temperatures in this zone preclude proper function of the dispersant. This leaves any dispersancy action down to the detergent additive in the formulation. The mixed salicylate detergent additive was better than the phenate/sulphonate detergent additive in this respect.

In the diesel sump the succinimide dispersant seems to perform much better than in the piston ring zone. The very low soot loading in the gasoline engine oil sump sample was too low to determine if this was also the case.

The improved performance exhibited by the salicylate may also be due to, in part, an additive synergy that might exist between the succinimide dispersant and the salicylate detergent but does not exist between the succinimide and the phenate/sulphonate detergent package.

One point to note is that the overall dispersancy performance of the oils did not, in general, get any better or worse over the course of the engine run. The old ring pack designs of these engines, with no low emissions criteria to fulfil have a relatively high lubricant replenishment rate through the ring pack of relatively fresh sump oil. A more modern low emission engine would not replenish the ring zone oil as quickly and would subject the detergent/dispersant package of the oil to a greater ring zone residence time^{2,3}, stressing the oil further. The sump oil, especially in a modern diesel engine would be expected to contain a great deal more soot. This already sooty oil for ring zone replenishment and higher residence time in the ring zone might show a decreasing dispersancy performance over time in the piston ring zone of a modern low emission diesel engine.

The experience the formulators have of which type of dispersant to use for certain applications is derived mostly from engine test experience, rather than any fundamental understanding of dispersant behaviour in the piston ring zone. Discussions with Castrol of the results revealed that the dispersant type used in this

matrix of oils was a variety that is commonly used in gasoline engine oil formulations. This would partly account for the improved ring zone dispersancy exhibited in the gasoline engine over the diesel engine. This discussion led to a second matrix of oils (Table 1-2) to be formulated with a succinimide dispersant type more commonly used in diesel engine oil formulations.

It should be noted that for further analysis of this technique, statistically designed experiment should be sought to examine the repeatability of this technique. This investigation makes no attempt to determine the repeatability of the modifications to the standard Blotter Spotter Test but it is expected the improvements described in this thesis would improve the repeatability of the Blotter Spotter Test.

Overall top piston ring zone dispersancy performance of the oils improved in the change from phenate/sulphonate to mixed salicylate detergent, in both gasoline and diesel engines, and was nominally independent of the dispersancy treat rate.

3.4 Conclusions from the Blotter Spotter Test

- Full dispersant treat not better than half dispersant treat in TRZ in either gasoline or diesel engine
- Full dispersant treat better than half dispersant treat in sump of diesel engine
- Mixed salicylate detergent acts with dispersant performance in the TRZ of gasoline and petrol engines
- Succinimide dispersant is overall, not effective in the TRZ of diesel or gasoline engines

3.5 Recommendations for Further Work

- A comparison of dispersant types, especially succinimide dispersants of different molecular weights
- Further development of the method, especially improving spot application with accurate automated liquid handlers or automated TLC spotters
- Comparisons of dispersant performance with respect to engine load and speed
- Investigations of other additive-dispersant interactions and impact on TRZ and sump dispersancy performance such as interactions between ZnDTP-dispersant and friction modifier-dispersant

With a suitably designed and statistically driven experiment, there is scope to transpose this method into a measure of remaining useful dispersancy of diesel engine oils. This can be applied to top ring zone oil samples or as a general engine test or field method for sump samples.

¹ Seifert, Measurement of Soot in Diesel Engine Lubricating Oil, *SAE* 951023.

² Cupples, S. D., et al, A Study of Lubricant Condition in the Piston Ring Zone of Single Cylinder Engines Under Typical Operating Conditions, *SAE* 881586.

³ Fox, M. F., et al, *Lubricant Mechanisms and Degradation in the Ring Pack of Operating Diesel Engines*, Annual Technology Development Contractors' Coordination Meeting, Dearborn, Michigan, 1994.

4 Particle Size Analysis.

4.1 Introduction

The 57 and 58 series oils from the first matrix of used oil samples (from both diesel and gasoline engines) were analysed by laser scattering particle size analysis. Following on from this a second matrix of oils was formulated using a dispersant type more commonly found in diesel engine oil formulations. This matrix of oils was only run in the diesel engine. The gasoline engine runs were omitted as, at this stage, the particle size analysis results were proving inconclusive for gasoline engine TRZ samples and the work was beginning to narrow onto diesel particulate in TRZ oil samples.

Soot loading was also measured (by thermogravimmetry) on the second matrix of used oils afterwards. Unfortunately the used oil samples for the first matrix were unavailable.

4.2 Laser Scattering Particle Size Analysis

4.2.1 Theory of Scattering

When a light wave is incident on a reflecting object much larger than the wavelength, the light will be scattered in all directions. However when a particular ray is incident at the edge of a particle then the ray will be deflected. If the beam of light has a diameter much larger than the particle it will be scattered in a cone, which is related to the size of particle. This is known as Mie scattering, Figure 4-1.

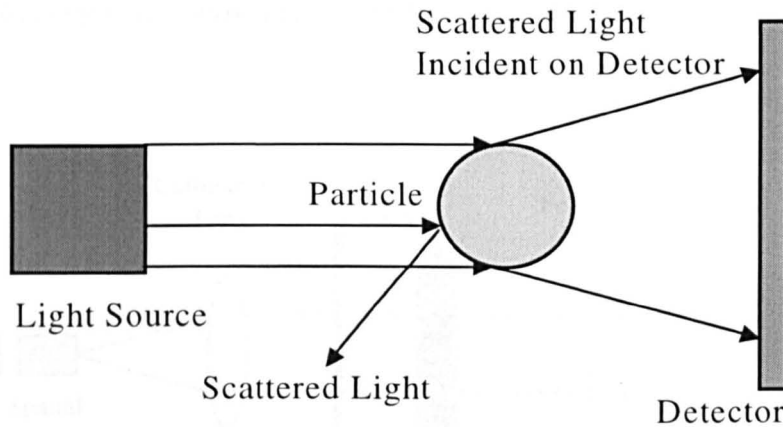


Figure 4-1 Mie Scattering of Laser Light¹

4.2.2 Malvern Mastersizer S

The instrument used to determine particle size distributions in this study was the Malvern Mastersizer S. This instrument uses a laser light scattering technique, which offers several advantages over conventional particle size techniques.

Figure 4-2 The Particle Sizer System¹

- No calibration is required as the instrument is based on fundamental physical properties (the instrument used in the study was certified by Malvern Instruments and used at their premises).
- It is non-intrusive using a low power laser to determine particle size.
- It is fast, requiring less than 1 minute to take a measurement and analyse it.
- It is simple and easy to use. Modular arrangement allows different types of sample to be introduced using a range of easy-to-handle measurement cells. There are no fine apertures to block.

The particle sizer system is shown in Figure 4-2.

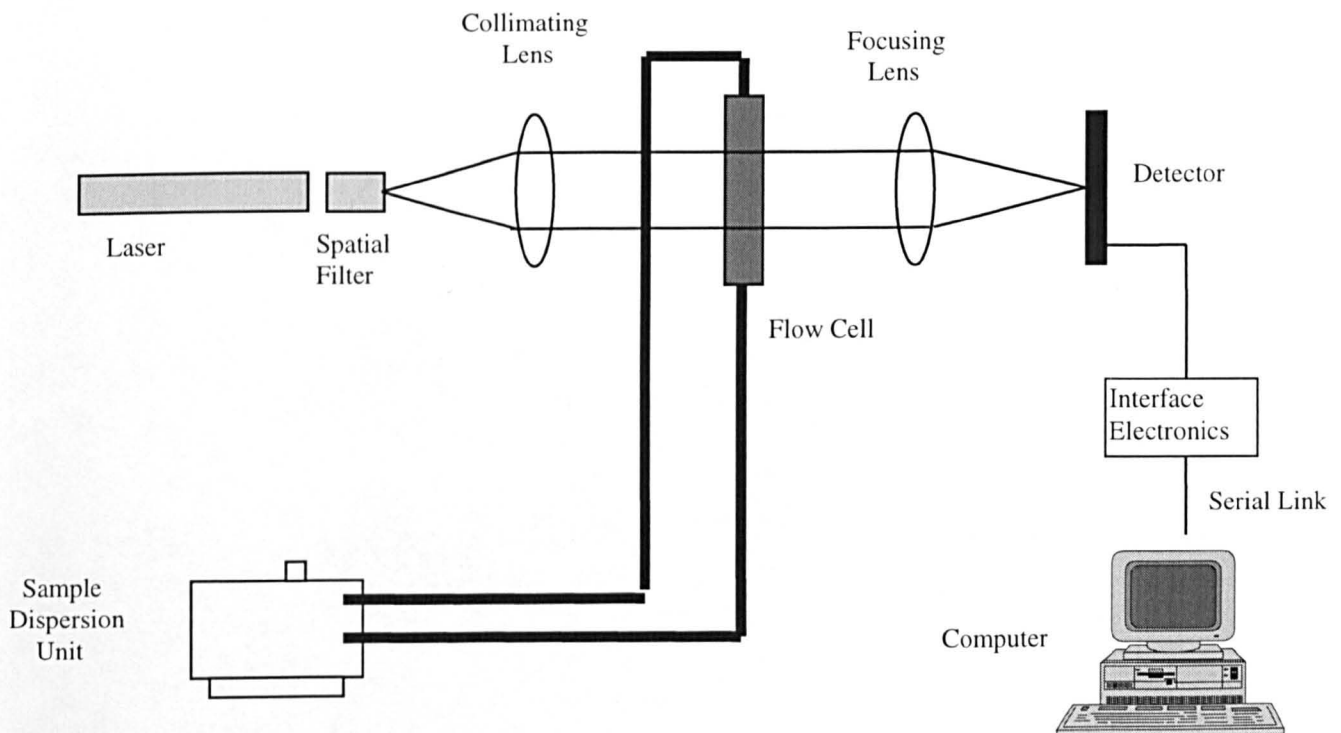


Figure 4-2 The Particle Sizer System¹

The Mastersizer S uses the principle of laser light scattering, which is a non-imaging technique. The instrument uses two optical configurations to cover the full range of particle sizes ($0.05\mu\text{m}$ to $1000\mu\text{m}$). The two configurations are conventional Fourier optics ($>0.5\mu\text{m}$) and reverse Fourier optics ($<0.5\mu\text{m}$)

4.2.3 Conventional Fourier Optics

The light from a low power Helium-Neon laser forms a collimated and monochromatic beam of light, maximum 18mm diameter. Any particles present in the beam will scatter the laser light. The scattered light and the unscattered remainder are incident on a receiver lens. This is the Fourier transform lens forming the far field diffraction pattern of the scattered light at its focal plane. A detector in the form of a series of angular sectors collects the scattered light over a range of angles, Figure 4-3.

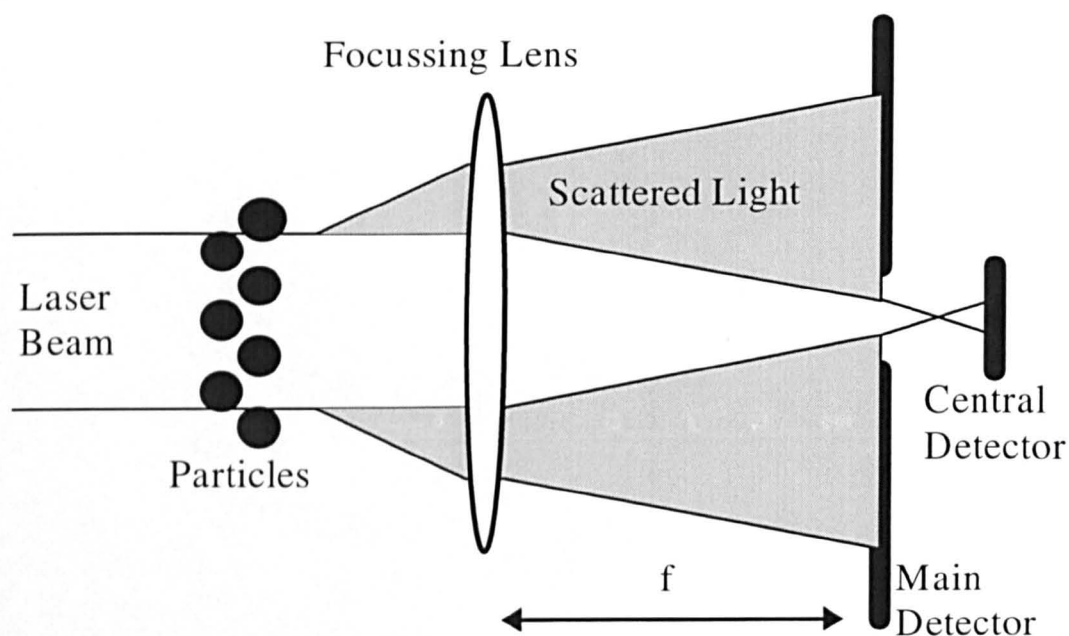


Figure 4-3 Conventional Fourier Optics¹

The unscattered light passes through a small aperture in the detector and out of the system. The total laser power passing out of the system in this way is monitored by the central detector allowing the sample volume concentration to be determined. This configuration also has the property that wherever the particle is in the analyser beam, its diffraction

pattern is stationary and centred on the detector, Figure 4-4. It also does not matter if the particle is moving in the beam since its diffraction pattern is always stationary.

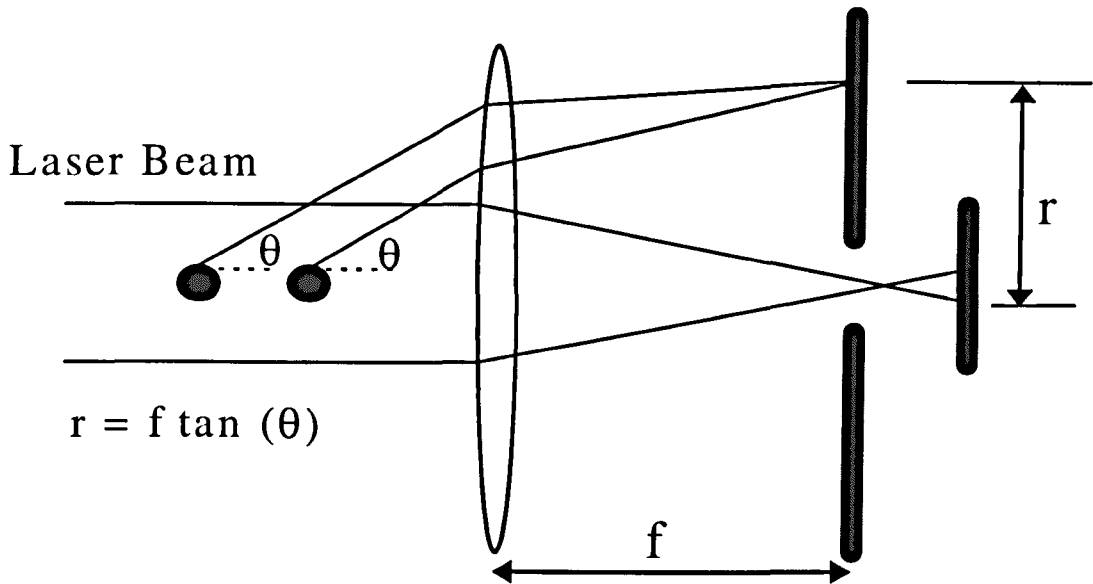


Figure 4-4 The Stability of the Diffraction Pattern¹

4.2.4 Reverse Fourier Optics

This configuration is needed for large scattering angles. Instead of forming a collimated analyser beam, the output beam is focused to a point in the plane of the detector. The sample cell is placed at a known cell distance (d) from the detector, Figure 4-5. In this configuration the diffraction pattern is still measured. The scaling constant is now the distance (d), not, as in the conventional configuration, the focal length (f). At any cell detector distance the diffraction pattern does not require focusing. As in the conventional configuration it does not matter where the particle is in the laser beam, the diffraction pattern remains stationary.

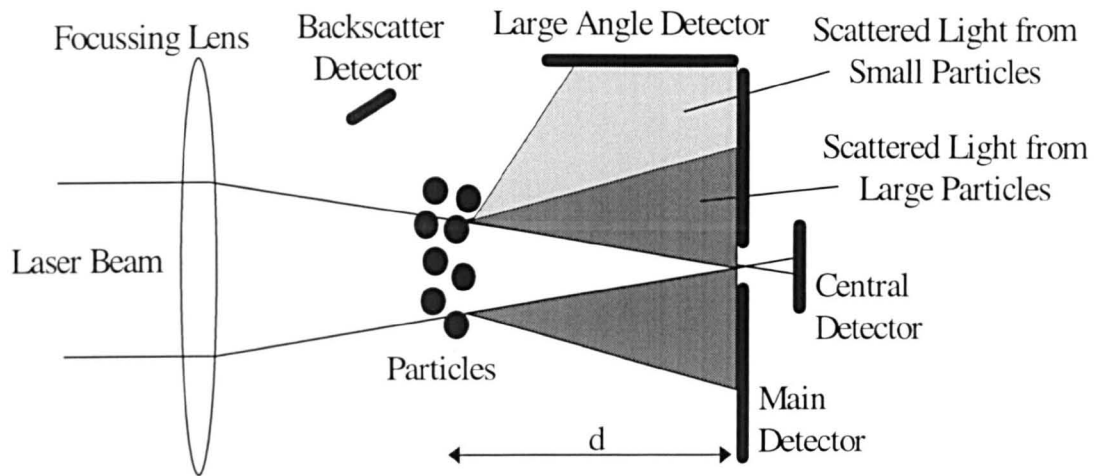


Figure 4-5 Reverse Fourier Optics¹

4.3 Soot Analysis by Thermogravimmetry

Soot analysis using thermogravimmetric analysis (TGA) is method used to determine the amount of soot (by weight) in a used oil sample. The procedure used is a modified version of the 'Enhanced Detroit Diesel TGA Procedure'^{2,3}.

4.3.1 Soot Analysis

The sample size used is approximately 4mg in a platinum sample pan.

The following temperature program is used for the soot analysis on the TGA:

1. Initial purge gas - Nitrogen at 80 l/min
2. Isothermal at 50°C for 1 minute
3. Heat to 550°C at 100°C per minute
4. Isothermal at 550°C for 1 minute
5. Heat to 650°C at 20°C per minute
6. Switch purge gas - Air at 80 l/min
7. Heat to 750°C at 20°C per minute

The program is considered finished once a stable weight residue remains unchanged for 5 minutes or longer. Soot is the difference in the weight plateaus at purge gas change, approximately 650°C, and after a stable weight residue is obtained around 750°C. The actual sample weight reported is the percentage of the total to the nearest 0.1 weight percent.

4.4 Methodology

All of the samples obtained from the engine runs (gasoline and diesel) of the first matrix of oil samples (Table 1-1) were analysed by laser scattering particle size analysis using a Malvern Instruments Mastersizer S particle size analyser using a 25ml small volume stirred cell, while the dilution solvent used was petroleum ether. The lower detection limit of the Mastersizer S in the configuration used was 0.5 μ m.

The samples obtained from the Petter AA1 diesel engine / second matrix (Table 1-2) combination were also tested for by the above method and also for soot content using a modified version of the 'Enhanced Detroit Diesel TGA procedure'.

4.4.1 Treatment of Results

The results from the particle size analysis are shown by the Mastersizer instrument as a distribution based on the total volume (%) of a particular size of particle assuming equivalent spheres. An example is shown in Figure 4-6.

Each of the sets of results for the different oils were then plotted against a third axis, run time for that sample. This was then represented as a 3D contour plot for each oil showing the particle size distribution for ring zone samples versus engine run time. An example of such a plot is shown in Figure 4-7.

Particle Size Dist. of 57a TRZ 300 mins.

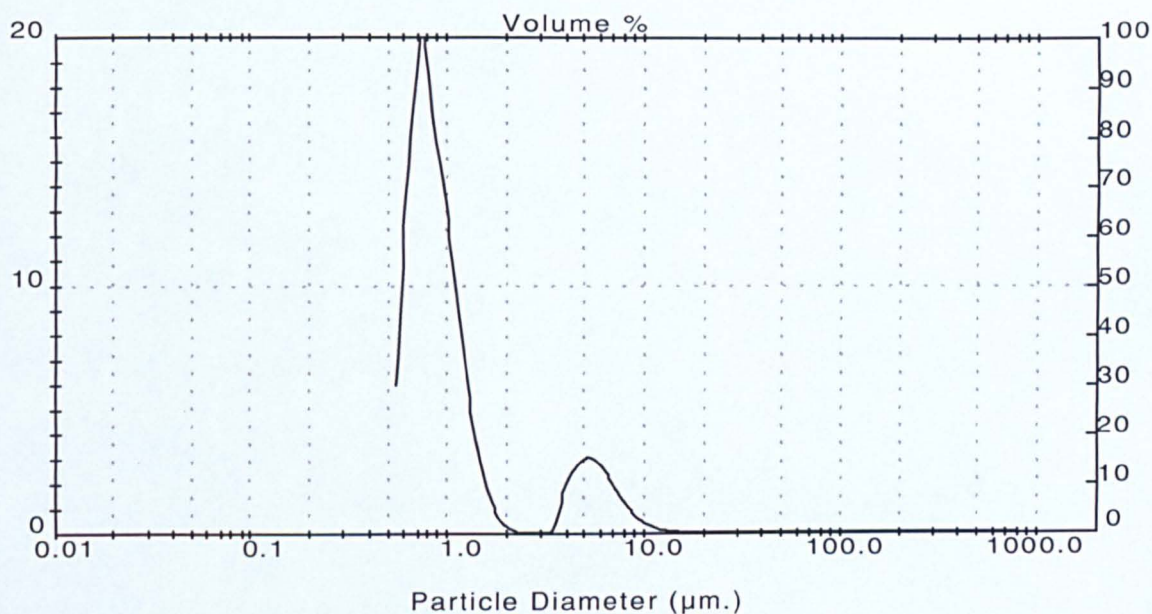


Figure 4-6 Example of Particle Size Distribution

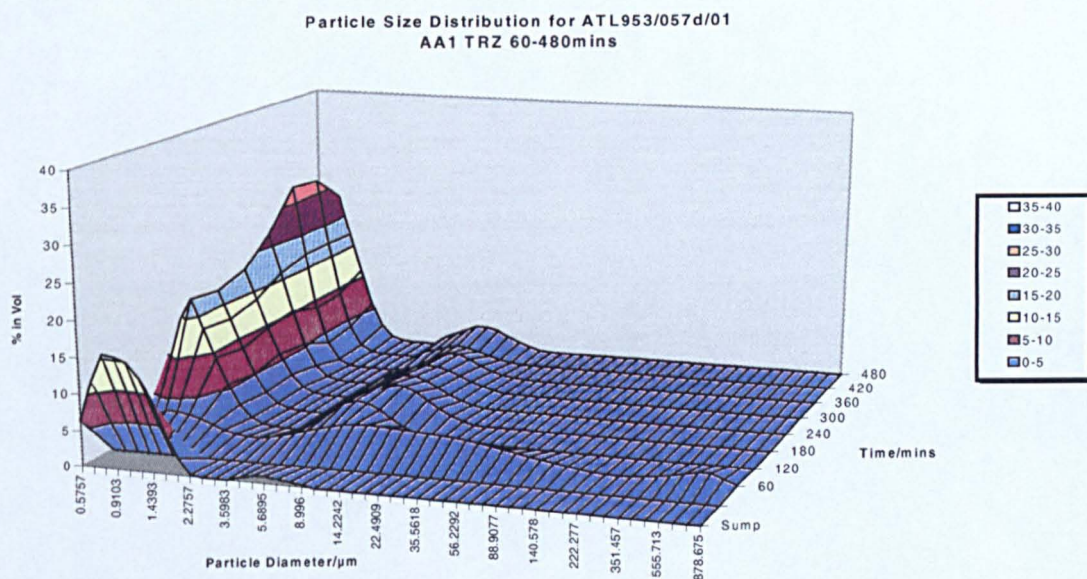


Figure 4-7 Particle Size 3D Contour Plot

At this stage, some consideration was also given to the mass of soot in each sample as well as the size distribution of the soot particles when comparing the changes in size

distributions over time⁴. The samples obtained from the Petter AA1 diesel engine / second matrix (Table 1-2) were tested for soot content using a modified version of the ‘Enhanced Detroit Diesel TGA procedure’.

It can be seen from a typical example of a particle size distribution for a top ring zone oil sample (Figure 4-6) that a distinct set of size bands occurs. The first, large, size band occurs at 0.7-0.8 μ m and represents the small initially formed soot. The second, smaller and wider, size band occurs at around 5-12 μ m and represents the first agglomeration of soots where the dispersant additive is acting ineffectively. Sometimes a third, larger agglomeration is seen at >15 μ m. This has led, finally, to graphically representing the changes in the height of each size band versus engine run time for each of the oil series. An example is shown in Figure 4-8.

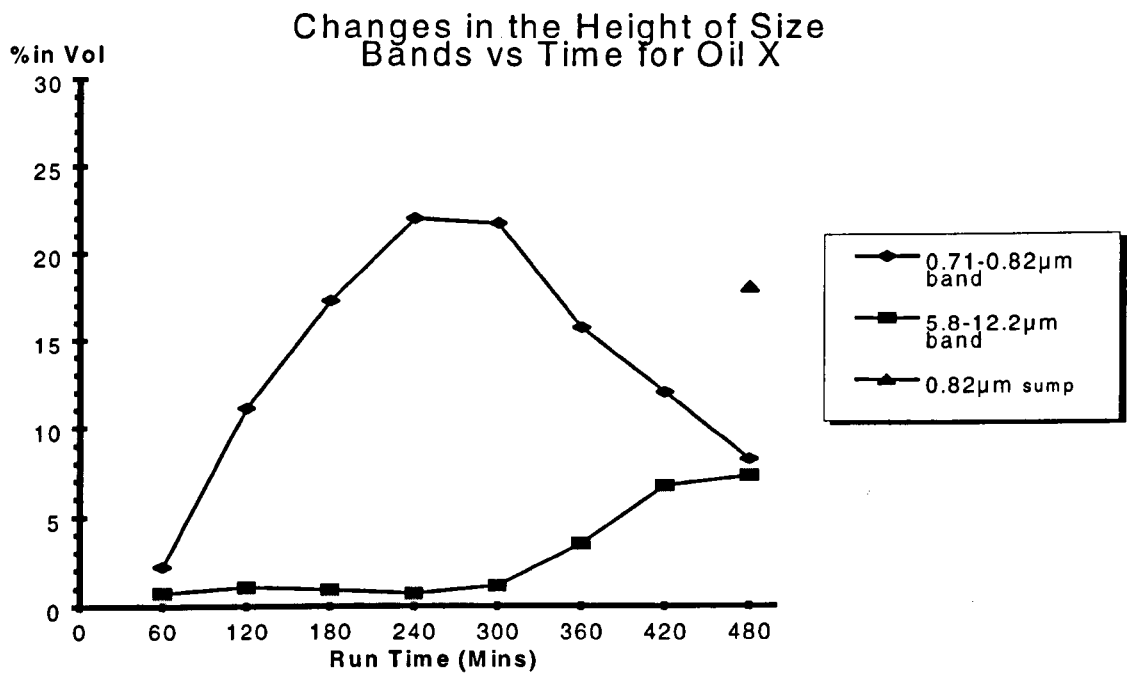


Figure 4-8 Example of Changes in the Height of Size Bands vs Time

4.5 Results and Discussion

All of the results for the particle size analysis are included in the appendices. The 3D contour plots for the gasoline engine oil samples are in appendix 1 and for the diesel engine samples in appendix 2. The graphs which show changes in the height of particle size bands for the first oil matrix are included in appendix 3 and for the second oil matrix in appendix 4. The TGA soot results are included in appendix 5.

4.5.1 W1 - First Oil Matrix

From observation of the particle size distribution 3D contour plots from the Petter W1 gasoline engine runs (appendix 1) it can be seen that conclusions are difficult to draw. The concentration of oil sample (20+ drops of oil in 25ml solvent) from that was required to obtain an adequate obscuration factor for the laser was too large. The software uses the refractive index of the diluent solvent in it's calculations. With large concentrations of lubricating oil then this changes enough to cause significant errors in the results. Coupled with the relatively small amount of particulate in the oil then the method fails to be useful for gasoline oil samples. The diesel oil samples only required 2-3 drops of oil to give good repeatable results due to the higher soot loading.

The technique is clearly not suitable for examination of particulate from the top ring zone of a gasoline engine. At this point the project solely concentrates on particle size distributions and morphology (chapter 5) in TRZ oil samples from the Petter AA1 diesel engine.

4.5.2 AA1 - First Oil Matrix

The contour plots (appendix 2) show that distinct particle size bands exist in all the series of approximately 0.7-0.8 μ m and 5-12 μ m in the TRZ and sump. To a lesser extent much larger particulate does exist but there are no observable trends. These larger particulate (15-75 μ m) are much less in number. Specific trends are observed in the 0.7-0.8 μ m and 5-12 μ m size bands.

The $\sim 0.8\mu\text{m}$ size band in the 57a/b/c oils (appendix 3) generally increased over the run showing the increased soot levels over time in this size but showed no overall tendency for growth into the larger particle agglomerations over time. 57a showed steady growth of the $\sim 0.8\mu\text{m}$ size band up to 360 minutes of engine run time, although there followed a sharp decrease in this size band to end of test and a small decrease in the larger size band. A very large size range exists (appendix 2) at $\sim 75\mu\text{m}$ in the end of test TRZ sample. At this size it would only represent very few particles of that size but it does indicate that the agglomeration to much larger particulate was very sudden.

The problem here is that if there was a large increase in soot loading in the final sample versus the sample before then the results could be difficult to compare. The results from the mastersizer are represented as percent volume of total particulate of a particular particle size. This means that a very large particle would relatively reduce the perceived volume of smaller particulate even though from one sample to the next there may be little change in the number of particles in a particular size range. Although unlikely, this could happen if an increase in soot loading from one sample to the next was mostly taken up by a new size range. It was for this reason that the individual soot loading (as measured by TGA) was taken into account for the different hourly samples for the second matrix of oils. At this earlier stage of the project the TGA soot method was not available to run the first matrix of oils.

57b with half treat dispersant shows a very steady rise in the $\sim 0.8\mu\text{m}$ size band, slightly declining medium size band and no other significant larger sizes, suggesting good dispersancy. 57c with zero dispersant has a large agglomeration ($\sim 40\mu\text{m}$) in the 120 minute sample which relatively reduces the heights of the other size bands. This larger agglomeration does not continue through the rest of the run suggesting it could be an anomalous result.

It must be noted that all of the size range results are tempered by any larger agglomerations, although the effect would only be severe in the reduction of the height of the size band if the other agglomerations were very large, as in 57a at 480 minutes and 57c at 120 minutes.

If the last few hours of the 57a run are disregarded then the 57a/b/c runs can be regarded as being broadly similar, indicating that the dispersant treat level has little effect on particle control. As with the blotter spotter results, it points to the dispersancy capacity of the detergent, rather than the dispersant, in these formulations in the piston ring zone of the diesel engine.

The sump samples for the 57a/b/c oils show very small amounts of the of larger size bands. They also show that the $\sim 0.8\mu\text{m}$ size bands are higher in the end of test sump samples than in the end of test top ring zone samples suggesting superior particulate control in the sump. This suggests the dispersancy effect of the dispersant comes into play in the sump where the lubricating oil is much cooler.

The 58a/b/c oils (appendix 3) show a more erratic trend. At full dispersant treat (58a), there is a gradual overall increase in the $\sim 0.8\mu\text{m}$ size band up to 300 minutes followed by a drop to the end of test with no increase in the levels of the medium size band. The drop in the $\sim 0.8\mu\text{m}$ size band at 180 minutes is due to an agglomeration that is evident at $\sim 50\mu\text{m}$. The smaller size bands in the 60 and 480 minute samples are also reduced due to larger agglomerates but in these cases the height of the larger agglomerate band is small but are very broad, spanning approximately the 10-30 μm size range.

58b and 58c show much more large agglomerations than the other samples in this matrix making it difficult to observe any growth trends in the small size band (they would be expected to be similar to 58a from the evidence of the 57 oil series) but clearly these oils are showing poor dispersant control by allowing large agglomerations of particulate to form.

The growth of the small size band over time in these samples are not at as steep a rate as the 57a/b/c oils but there exists very much more very large particulate in the 58a/b/c oils. The sump samples for the 58a/b/c oils show the same trend as the 57a/b/c/ oils.

4.5.3 AA1 – Second Oil Matrix

The contour plots for 57d/e/f are shown in appendix 2. In 57d the 60 minute sample shows no distinct size bands at all. There is no $\sim 0.8\mu\text{m}$ size band but just one long continuous size range from 0.5 to $875\mu\text{m}$ suggesting that this is an anomalous result. Otherwise in the rest of the engine run this oil shows good particulate control showing a steady growth in the $0.8\mu\text{m}$ size band and a relatively constant 5- $12\mu\text{m}$ size band.

57e shows that the medium size band centred around $8\mu\text{m}$ has a broader range than those seen in 57d. Nevertheless the growth of the small particle size band is similar. There is a larger distinct agglomeration ($\sim 40\mu\text{m}$) in the 180 minute sample. This shows that the half treat dispersant oil has a slightly weaker control of particle size than the full treat oil.

The zero treat dispersant oil (57f) shows a very distinct trend. The smaller size band increase sharply from the beginning of the test to 240 minutes and then sharply declines to the end of test. This is at the same point that the medium size band has begun (after decline from the beginning of the test to 240 minutes) to increase sharply and almost linearly until the end of test. This is a classic example of smaller particles steadily agglomerating into larger particles in the piston ring zone in the absence of any residual dispersancy.

All of the 57d/e/f and 58d/e/f sump samples show very good particulate control.

58d shows some large agglomerations ($\sim 15\mu\text{m}$ at 60 minutes and $\sim 50\mu\text{m}$ at 120 minutes) in the first two hours of test, which causes the relatively steep apparent rise of the smaller size band up to 180 minutes. The rise in this band is not so steep for the rest of the run. Apart from those two larger agglomerations at the beginning of this run the results show steady particle size control for the rest of the run.

In the half treat dispersant oil (58e) a similar effect is seen to that observed in the 57f sample. After a sharp initial rise of the smaller size band it declines for the rest of the test but is mirrored by a steady increase in the medium size band. The 58f sample shows better control with a steady rise of the smaller size band and a broad range in the medium size band.

One general observation from all the engine runs is that the particulate accumulated in the piston ring zone as the engine warms to operating temperature in the first hour of running tends to be of less distinct size ranges. There is usually a smaller $\sim 0.8\mu\text{m}$ size band (than the rest of the engine test) but a much broader distribution of medium to large particulates. This is inevitably down to the dispersant / detergent package not working at optimum temperature and is probably caused in the first few minutes of the first hour of the test.

The size of particulate observed around $\sim 0.8\mu\text{m}$ is most often described by the literature as the first agglomeration of primary soot particles. These size ranges observed are engine specific but do fall into general categories. Kittleson⁴ described the first agglomeration of particles from 0.12 to $0.27\mu\text{m}$ and further agglomerations near to $1\mu\text{m}$. Colacicco⁵ described the primary soot particles involved in agglomerations at $0.03\mu\text{m}$ and the agglomeration at $0.4\mu\text{m}$. Gautam⁶ and Kawamura⁷ described the primary particles at $0.02\mu\text{m}$ and the first agglomeration at up to $0.5\mu\text{m}$. Sato⁸ observed the primary particulate also at $0.03\mu\text{m}$ and the first agglomeration at $0.15\mu\text{m}$. Finally, Mainwaring⁹ only described particulate as ranging from 0.03 to $0.1\mu\text{m}$. All of these researchers, however, were testing oil samples derived from the sump sample of different engines and, as we have seen, unregulated particle growth above the first agglomeration is not evident in this region. Particulate agglomerations over $1\mu\text{m}$ are also evident in the top ring zone.

4.6 Particle Size Analysis Conclusions

The case of the observed sudden appearance of $\sim 75\mu\text{m}$ particulate and reduced volume of particles in the $\sim 0.8\mu\text{m}$ and $\sim 5\text{-}12\mu\text{m}$ size bands is direct evidence of particle agglomeration and breakdown of dispersant control in the piston ring zone. This also shows that agglomeration does not necessarily linearly proceed from $\sim 0.8\mu\text{m}$ to $\sim 5\text{-}12\mu\text{m}$ to $+15\mu\text{m}$ but can proceed from $\sim 0.8\mu\text{m}/\sim 5\text{-}12\mu\text{m}$ to $+15\mu\text{m}$ size particulate where poor dispersancy is exhibited in the piston ring zone. This effect is also seen in the 58a/b/c oils.

The 57a/b/c oils versus the 58a/b/c oils suggest that dispersant treat has little difference on particulate agglomeration control. With this test, however, the phenate/sulphonate detergent (57 series) seems to act with better dispersancy than the salicylate detergent (58 series), which is in opposition to the conclusion from the blotter spotter tests that the salicylate showed better dispersancy than the phenate sulphonate.

¹ Dawn Chescocoe and Peter J. Goodhew (1990). *The Operation of Transmission and Scanning Electron Microscopes*. Royal Microscopical Society Microscopy Handbooks, no. 20. Oxford University Press, Oxford.

² Graham Lawes (1987), *Scanning Electron Microscopy and X-Ray Microanalysis*, John Wiley & Sons, Chichester.

³ Andy Baker, *Atomic Force Microscopy*, <http://teddy.phy.bris.ac.uk/spm/techniques/AFM.html>

⁴ P.J Shuff and L.J. Clarke *Imaging of lubricating oil insolubles by electron microscopy* Tribology International Volume 24 No. 6 Dec. 1991 pages 381-387.

4.7 Recommendations for Further Work

- Development of technique to include gasoline engine oil derived samples. Could be achieved by removal of particulate from the bulk sample by centrifuge, dissolving the oil in a solvent, centrifuge, decant, further solvent dilution, centrifuge etc. There would probably only be enough in a sump sample to achieve enough particulate to introduce to the Mastersizer. Another possibility is development of a thin film cell with no solvent dilution.
- Taking into account engine running parameters with the particle size results and using multivariate analysis techniques may help to elucidate further trends in particulate agglomerations.
- Different detergent / dispersant package chemistries and the effect other additive - additive interactions and their effect on dispersancy in the piston ring zone.
- Representing the particle size distributions in terms of relative number of particles in a size band over time rather than volume%. This would remove the ambiguities that arise with using volume% where other very large agglomerations exist.

5 Electron Microscopy Techniques.

5.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX)

5.1.1 Theory of SEM

The resolution of the optical microscope is limited by the wavelength of light, typically 500 nm. Using electrons, with wavelengths of around 0.1 nm^1 , much better resolutions can be obtained.

Electrons are emitted from a hot cathode, and are accelerated towards the sample by applying a voltage, in the order of kV to the anode. The beam of electrons is focused, using magnetic lenses, to a small spot on the surface of the sample. This spot is scanned over the surface by deflecting the beam with scanning coils, just as electrons are deflected in a television cathode ray tube.

A schematic of the SEM is shown in Figure 5-1. Electrons are emitted from the electron gun, and are focused on to the sample through the lens. Electrons scattered from the surface of the sample are monitored by the detector, amplified and passed to the display. The scan generator is used to create the waveforms for controlling the beam deflection, which is passed to the deflection coils.

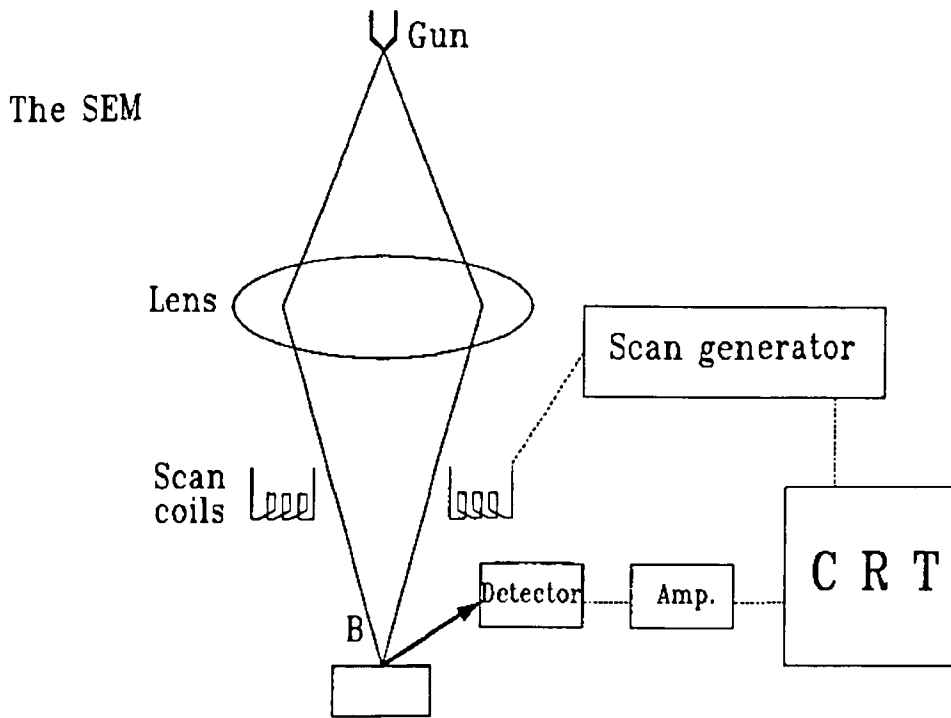


Figure 5-1 Schematic of SEM, Showing Primary Components

Figure 5-2 shows the thermionic electron gun. The filament current controls the amount of electrons emitted from the surface of the filament. This should be set to obtain the maximum possible emission, where the emission becomes saturated. The bias / emission controls the total beam current, which affects the brightness of the image. The HT is the accelerating voltage for the electron beam. This is varied depending on the sample being imaged. A higher accelerating voltage penetrates further in to the sample, but generally gives less contrast in the image.

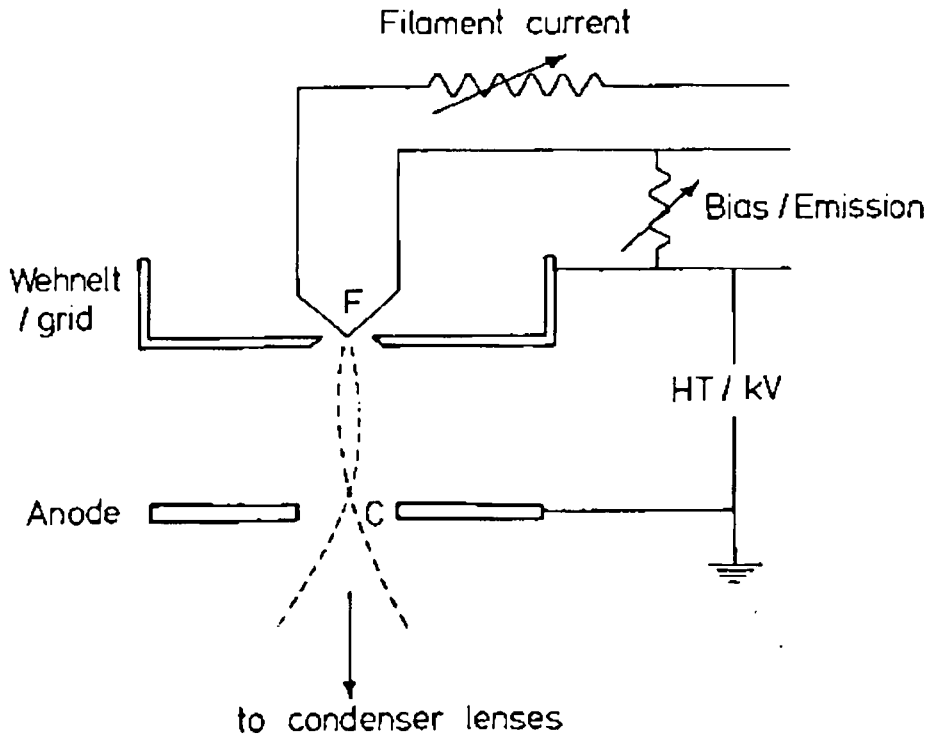


Figure 5-2 Thermionic Electron Gun in an SEM

Electrons emitted from the surface of the sample can be observed with a detector. Most SEM's have a detector for secondary emission electrons. Secondary emission electrons are loosely bound conduction electrons from the sample, which are knocked out, by the incident beam electrons. Secondary emission electrons are widely used for topographical imaging. They are detected with a scintillation detector positioned behind a metal mesh, which is used to attract or deflect low energy electrons. A positive bias will attract electrons, allowing secondary emitted electrons to reach the detector without having to be in line of sight. A negative bias on the mesh will repel low energy secondary emitted electrons, allowing only backscattered electrons to reach the detector.

Backscattered electrons are electrons from the main electron beam, which have been deflected through angles approaching 180 degrees. These can be detected using the secondary emission scintillation detector with a negative bias, as described above, or more effectively by using a dedicated solid state detector positioned above the sample. The detector is normally circular, and has a hole in the centre which allows

the electron beam to pass through the centre, and detects electrons which have been reflected back in the direction of the electron beam through an angle given by the diameter of the detector and its distance from the sample.

Commonly, an SEM also has an X-ray detector, which can detect characteristic X-rays, emitted from the sample. This is usually a semiconductor detector, mounted as near to the sample as is possible. X-ray analysis is used on the SEM for element characterisation of the surface of the sample.

An essential part of the electron microscope is the vacuum system. This is needed for two reasons; firstly to prevent the electron beam from being scattered by air molecules, and secondly to minimise contamination on the sample and instrument. Contamination in the microscope may lead to deterioration in performance. The pressure inside the vacuum chamber is typically 10^{-4} Torr.

5.1.2 Theory of EDX

When high-energy electrons are incident on a surface, the energy from the electron can be converted in to electromagnetic radiation in the form of x-rays. Electrons from the electron beam landing on the surface of a sample is an example of where this happens, and the x-rays emitted from the normal operation of SEM imaging can be used to provide information of the chemical composition of the sample².

Electrons from the beam are able to ionise atoms on the surface of the sample. This ionisation is not necessarily caused by removing an outer, loosely bound electron. The electron may be removed from an inner electron if the beam energy is high enough. When such an electron is removed, the atom is left in an excited state, which then returns to the ground state as electrons fall to lower energy states. Electromagnetic radiation is released in this relaxation process, with a wavelength proportional to the energy gap between the electron energy levels in the atom. The electron energy levels are characteristic of a particular element, so the wavelengths of the emitted x-rays can provide information on the elements present at the surface of the sample.

5.2 Atomic Force Microscopy (AFM)

5.2.1 Theory of AFM

Atomic force microscopy is a scanning probe microscopy technique developed from scanning tunnelling microscopy (STM). There are many similarities between the STM and AFM. Like the STM, the AFM uses a local probe to scan the sample surface in a raster scan, controlled by piezo-electric motors, which can position the tip to sub-angstrom resolution. For STM operation, quantum mechanical tunnelling allows electrons to tunnel through the potential barrier between the tip and the sample. As the STM tip scans the surface, it measures the current passing through the tip, giving a signal proportional to the local electron density of states. The AFM does not rely on tunnelling, but measures the intermolecular force between the tip and the sample.

One of the reasons for the success of the STM is that the electron probability density function decays exponentially in to the potential barrier. This negative exponential function gives a significant change in tunnelling current for a given change in height. As can be seen from the intermolecular force curve in Figure 5-3, the gradient of the repulsive force at close separations is very steep, giving a large change in force for a small change in separation distance. This is the key to the success of AFM.

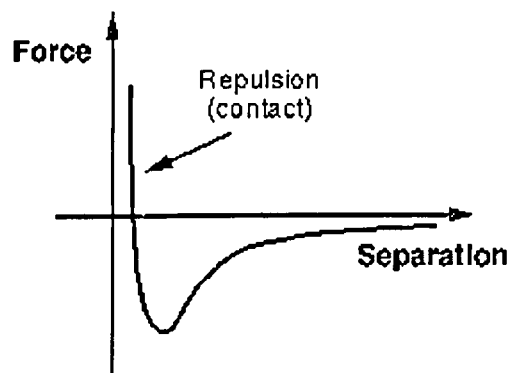


Figure 5-3 Intermolecular Force versus Separation Distance.³

The tip is mounted on a cantilever, and laser light is reflected from the cantilever to a split photodiode. The difference between the signals A and B gives a measure of the bending on the cantilever, and subsequently the force between the tip and the sample. This is shown in Figure 5-4.

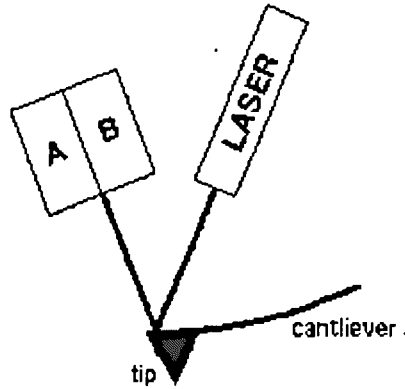


Figure 5-4 Tip, Cantilever and Optics for an AFM

There are parallels between the constant height and constant current modes of operation in the SEM and the operating modes of the AFM. The AFM can run in constant height mode, where the tip is scanned over the surface and changes in the force detected, and constant force mode, where the force is kept constant by a feedback control system and the height is measured from the amount of correction needed to maintain the constant current.

5.3 Transmission Electron Microscopy (TEM)

5.3.1 Theory of TEM

The principles of TEM are similar to SEM, differing in where the detector is placed with respect to the sample. In the SEM, the beam is incident on the surface of the sample, and backscattered and secondary emitted electrons are detected using detectors above the sample. In TEM, the electron beam passes through a very thin sample, and electrons are detected using a detector positioned beneath the sample. The geometry of the TEM is similar to the geometry of a conventional optical microscope, where a light source illuminates the sample and is positioned so that the light passes through the sample. Figure 5-5 shows a comparison between a conventional optical microscope and a TEM.

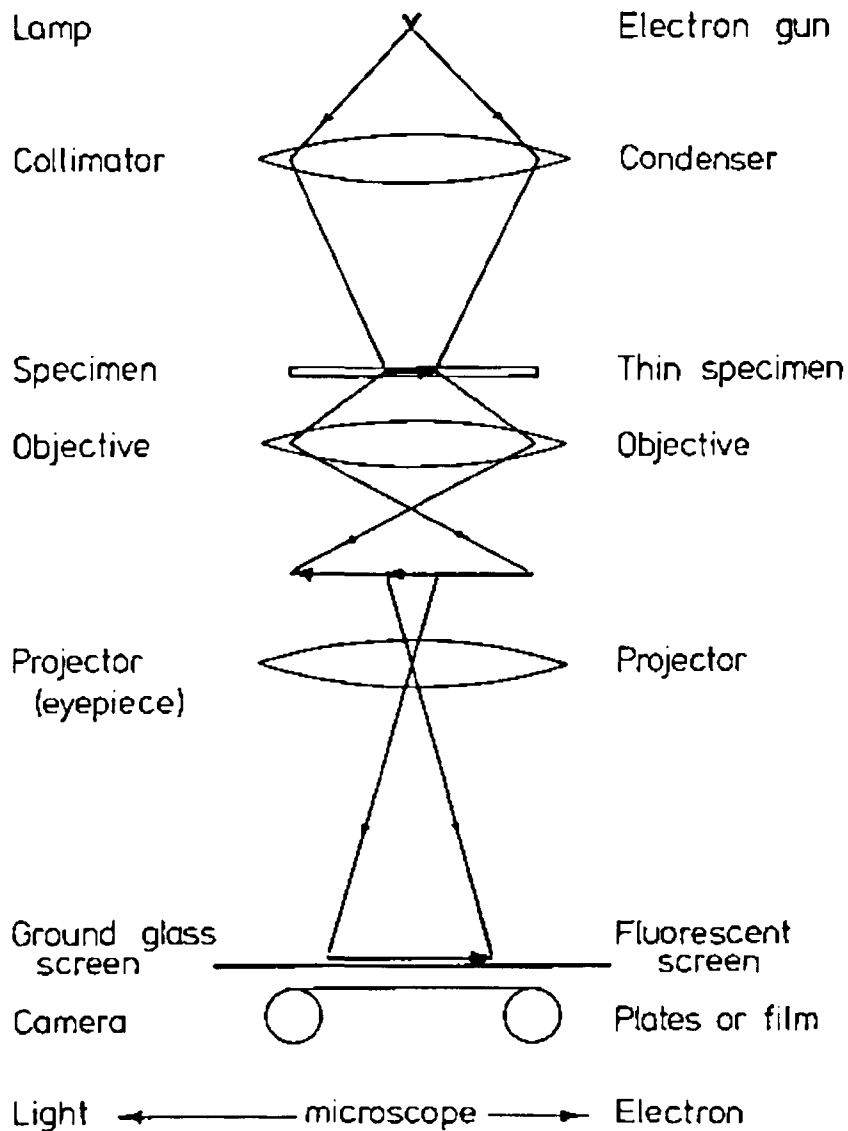


Figure 5-5 Comparison Between a Conventional Optical Microscope and TEM

The TEM can provide information about the sample, which the SEM cannot provide. The SEM gives information about the surface of the sample, whereas the electrons in the TEM pass through the sample and can give information throughout the thickness of the sample.

5.4 Development of Experimental Methods

5.4.1 SEM Imaging Methods and Oil Sample Preparation

A sample, which is to be imaged in the electron microscope, must first be mounted on a suitable, conducting substrate. This is placed on an aluminium microscope stub that fits in to the microscope. The aluminium stub can simply be used as the substrate, but the rough surface can make it difficult to see the sample. A common choice for a substrate used at De Montfort University is a small square of silicon wafer, which conducts well enough for most purposes, is extremely flat, featureless and very pure. The oil sample used throughout the work in this chapter was the 480 minute sample of 57f from the top ring zone of the AA1 diesel engine as described in the previous chapters

Any substrate that is used to mount the sample must have a good electrical connection to the stub. If the sample or substrates are not conducting enough, the area being examined will charge. This will tend to deflect the electron beam from the sample making the image dark. A good contact can be obtained by using conducting silver paint to adhere the surface of the substrate to the stub. If the resistance of the sample, or the conduction path from the sample to the stub is high, the stub and sample assembly can be coated with a thin film of metal.

The most commonly used method is to sputter gold on to the surface. The stub, with the sample on the surface, is placed in an evacuated container, and a small amount of argon is introduced. A bias, in the order of 1kV is set between the sample and a metal (gold) target, the target being negative with respect to the sample. The argon is ionised to form Ar^+ , which is accelerated towards the target. Ar^+ ions hitting the target eject particles of metal, some of which will land on the sample.

A second method of coating the sample is to evaporate a metal, typically aluminium, in a vacuum. If a non-conducting substrate is used, such as glass or plastic, the sample must be coated with metal.

5.4.2 Separating Particulates from Oil

Before any electron microscopy techniques can be used, the particles must be separated from the oil sample. This is particularly important in the case of the SEM, where the sample has to be placed in a vacuum chamber. Engine oil evaporating in the vacuum chamber will give poor results and could damage the instrument.

Immersion of a Carbon Coated Microscope Grid in the Oil Sample.

This is one of the techniques suggested by P. J. Shuff et. al.⁴. The particles are removed from the oil by immersing a carbon coated copper microscope grid in the oil and washing with solvent.

Very few particles were found on the grid when examined by SEM. A carbon coated nylon grid was used instead of a carbon coated copper grid for this experiment. This may have increased charging on the sample, preventing the imaging of the smaller particles, which would be expected to be observed using this method. However, the higher resolution images should have indicated the presence of these particles, even if the picture quality was poor, but none were found.

Filtration.

Attempts were made to separate out the particles by filtering the oil. A 0.8 μ m filter was used in a 25 ml Millipore filter funnel connected to a vacuum pump. A single drop of oil was dropped on to the filter paper and was washed through with petroleum ether under vacuum. The oil was washed through, leaving a deposit of soot particles on the filter.

Sample filter papers were imaged using the SEM. The filter paper was mounted by simply sticking on to an aluminium stub with double-sided sticky tabs. It was found that the filter paper charged quickly, giving poor results. Sputtering with gold successfully prevented charging, and good images of the surface of the filter paper were obtained. An example is shown in Figure 5-6.

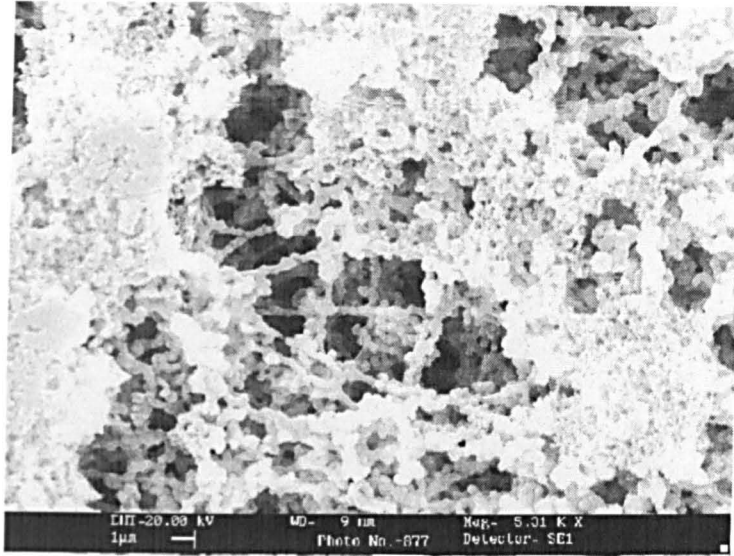


Figure 5-6 Gold Coated Filter Paper Imaged with SEM

The number of particles on the surface of the filter was small. Only the larger particles, (greater than $50\text{ }\mu\text{m}$) could be seen. Smaller particles were lost in the detail on the surface of the filter paper. Attempts to increase the number of particles on the paper by using more of the oil sample when filtering caused the filter to become blocked with soot, giving a solid black surface to the filter paper, which revealed no detail.

To overcome the problems with losing the detail of the particles in the complex structure of the filter, the filter paper was shaken over a clean glass microscope slide, which was then examined under the SEM. Some particles were seen on the slide, but with the small number seen, it is difficult to be certain that they were from the oil. The glass slide was gold sputtered before placing in the microscope. An image of some of the particles seen is shown in Figure 5-7.

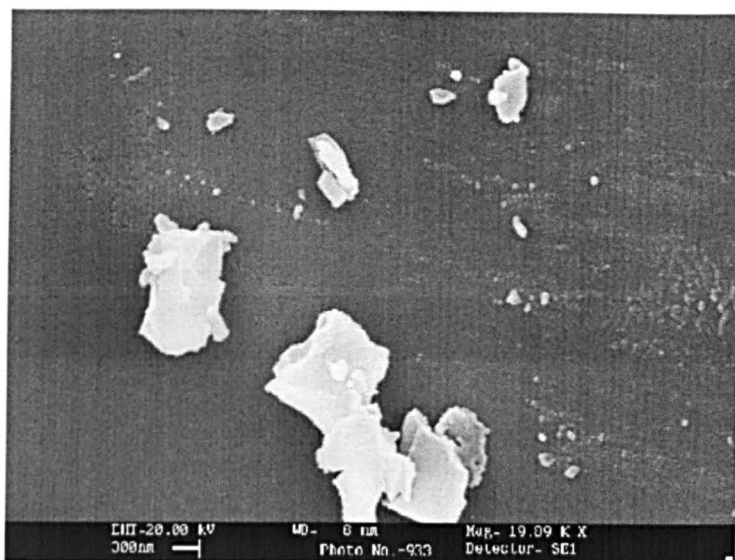


Figure 5-7 Image of Particles on Glass Microscope Slide that has been Gold Sputtered

Filtration Using An Ammonium Chloride Pack.

A filter was made by packing a syringe with ammonium chloride powder. Ammonium chloride sublimates at 304°C , and so can be removed by heating. The oil was dropped on to the top of the filter pack and then washed through with heptane. The oil was washed through, leaving some soot on the top of the filter. The top layer of the filter was removed and placed on an aluminium stub, which was heated to evaporate the ammonium chloride.

A very small amount of the particles were trapped with this method, most of the particles are washed through the filter. Attempts to grind the ammonium chloride to a finer powder to trap more particles were unsuccessful, the particles still washed through the filter. The technique also requires that the stub is heated to evaporate the ammonium chloride, which may alter the sample.

Electrostatic Techniques.

An electrode made from a single strand of wire was put in to a sample of particles in petroleum ether. The other end was connected to a d.c. power supply and 30V applied. The effect was very small, and only two or three particles were seen to be attracted to the tip of the wire when viewed through a microscope. The wire was

sharpened in an effort to increase the electric field at the tip of the wire, but had little effect. Both positive and negative voltages were applied, and a large flat electrode of opposite potential to the tip was tried, both inside and outside the container holding the sample. None of these experiments gave any significant improvements. The methods were also tried on the original oil sample containing particles before centrifuging, also with poor results.

Separation Using A Centrifuge.

By far the most successful method was to separate the particles from the oil using a centrifuge. An ordinary bench top centrifuge was used which was capable of speeds of up to 6000 rpm. Centrifuging the oil without first mixing it with petroleum ether does not give any separation, so about 1 cm³ of sample is put in to the centrifuge tube and mixed with petroleum ether to fill the tube to approximately 2/3 full. The actual amounts of sample and solvent are unimportant, as the technique does not provide a quantitative sample. The mixture of solvent and oil sample is then centrifuged at 6000 rpm for 5 minutes, and some separation of the particles can be seen. The oil and solvent mixture is then removed from the tube, leaving the concentrated particles in the tube. More solvent is added, and the process is repeated until only particles in solvent remain. About six repeats are necessary to dilute the oil sufficiently for SEM work. The best indication is to compare the colour of the centrifuged sample to the colour of petroleum-ether. It was found that if no colour difference can be seen between the petroleum-ether and the sample, successful images could be obtained with the SEM.

5.4.3 Mounting Particulates on a Substrate.

The methods described relate to mounting a sample, in the form of soot particles in solvent, on to a suitable substrate for SEM imaging. It is assumed that the particles have been separated from the oil by the method described previously (separation using a centrifuge).

Mounting Directly On An Aluminium Stub

The surface of an aluminium microscope stub is roughly machined, making it difficult to see any particles on the surface under an SEM. The aluminium stub was polished using fine sandpaper to give a clearer image. After cleaning with petroleum ether, the sample is dropped on to the stub and allowed to evaporate. The stub is then mounted in to the SEM with no further preparation. Some particles were seen on the surface of the stub, and it is possible that these are soot particles from the oil sample. Figure 5-8 shows some particles on the surface of the stub. Lines can also be seen on the stub where it has been polished.

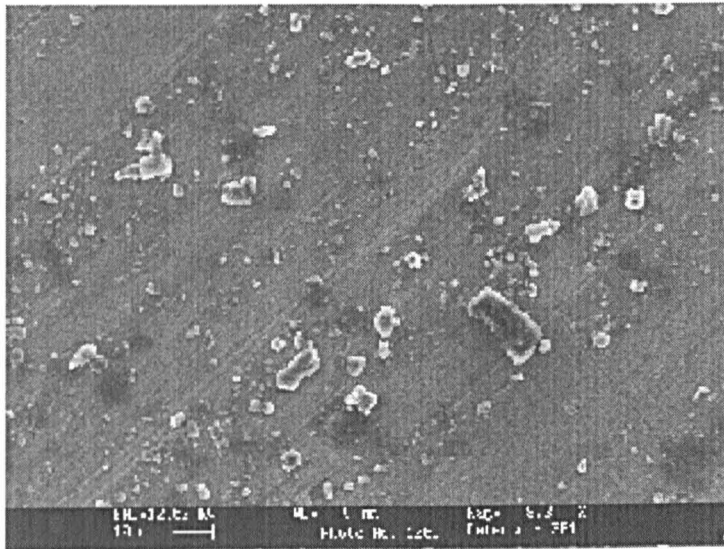


Figure 5-8 Particles on the Surface of an Aluminium Stub

It is difficult to say with any certainty that the particles shown in Figure 5-9 are from the sample because the surface of a 'clean' aluminium stub also shows surface details which could be seen as particles.

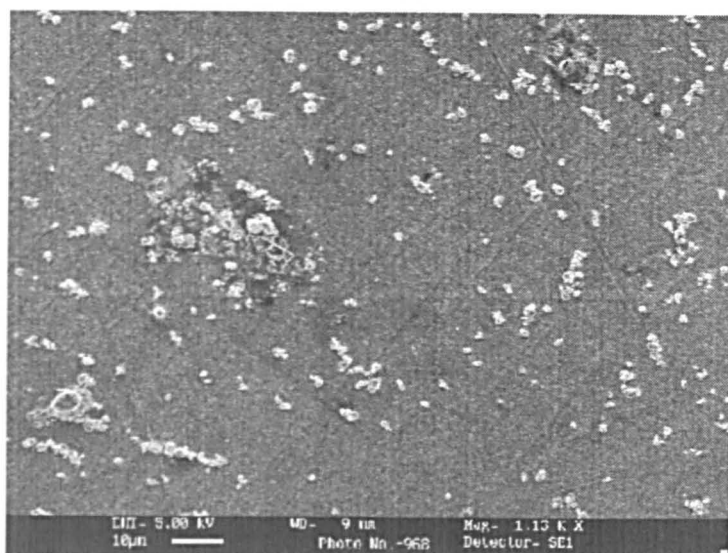


Figure 5-9 Clean Aluminium Stub

Mounting On Silicon

A square of silicon wafer, approximately 5mm on each side is stuck to the top of an aluminium stub with double sided sticky tabs. Silver paint was used to give a good contact between the surface of the silicon wafer and the aluminium stub. A few drops of the sample were dropped on to the surface of the silicon and the solvent allowed to evaporate. This was then mounted in the SEM.

The samples prepared by this method gave some good results, however the particles soon charged up, reducing the image quality, especially with the smaller particles. The silicon substrate proved to be very flat and featureless however, making it an ideal substrate in this respect.

Mounting On An Aluminium Cold Stage Stub.

Some of the sample was dropped on to an aluminium cold stage stub, which appeared to have a flatter surface than the aluminium stubs normally used, however, irregularities on the surface of the stub still made it difficult to see the particles. An image of the cold stage stub with particles on the surface is shown in Figure 5-10.

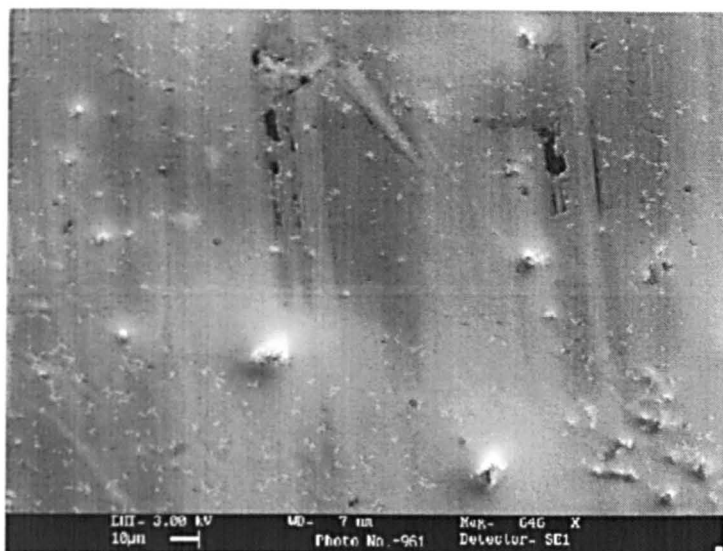


Figure 5-10 Particles on a Cold Stage Aluminium Microscope Stub

Mounting On Transparent Plastic Film.

A 5 mm wide strip of transparent plastic film cut from an overhead projector slide was dipped in to the container containing the particles in solvent. It was found that the particles stick to the film very well, and is a good way of removing the particles from the solvent and getting them on to a substrate. The end of the strip is then cut off , leaving a square of approximately 5mm on each side, which is stuck to an aluminium stub using double sided sticky tabs. Because the substrate is non-conducting, the stub, with the film and sample stuck to it is sputtered with gold. This method gave excellent results. Figure 5-11 shows particles from the oil on the flat plastic film surface.

Images were also taken of a piece of plastic film, which had been dipped in petroleum ether, and gold sputtered and appeared blank.

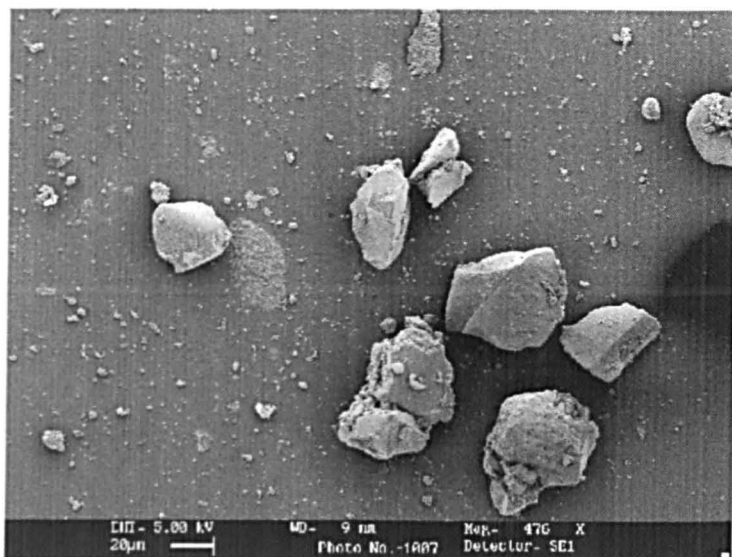


Figure 5-11 30µm Particles mounted on Transparent Plastic Film and Coated with Gold

Samples prepared on a square of silicon wafer could of course be gold sputtered to reduce charging, but the advantage of the plastic film method is that the particles readily stick to the surface. The film can be used to extract the particles by simply dipping it in to the sample. If this is done with silicon, no particles stick to the surface. To get particles on to the surface of silicon, the sample has to be dropped on to the surface and allowed to evaporate, and much fewer particles are seen than when film is used.

5.4.4 Mounting Particles For EDX Analysis.

Mounting On Plastic Film.

EDX was tried on the sample prepared on transparent plastic film. Although this sample gave excellent images, very little was gained from the EDX data because the large amount of gold measured obscured any peaks of other elements. Many of the elements, which may have been present in the sample, were further obscured by having X-ray energies near to the energies of gold transitions. This shows that any method of mounting the samples, which includes gold sputtering, is unsuitable for EDX measurements.

Mounting Directly On An Aluminium Stub.

The aluminium stub was polished with fine sandpaper to give a flat substrate and to remove the surface oxidation. The stub is then cleaned thoroughly with petroleum ether. A few drops of the sample were dropped on the stub and allowed to evaporate.

EDX scans of particles showed Al, Bi, Si, Pb, Ca, Cu and Fe. Scans of blank areas of the stub showed Al as expected, but also significant quantities of Cu and Fe, showing that the aluminium stubs are not pure enough for EDX work.

Mounting On Silicon.

A square of silicon wafer, approximately 5 mm on each side was stuck to the top of an aluminium stub using double sided sticky tabs. A good contact was made from the surface of the wafer to the aluminium stub using silver paint. After cleaning in solvent, a few drops of the sample were dropped on to the surface of the wafer and allowed to evaporate.

EDX scans of blank areas of the wafer showed only silicon, with no other elements present. Scans of particles gave good results, showing O, Na, Mg and Ca. These results show that silicon makes a very good substrate for EDX analysis. A spectrum obtained from a blank part of the wafer is shown in Figure 5-12.

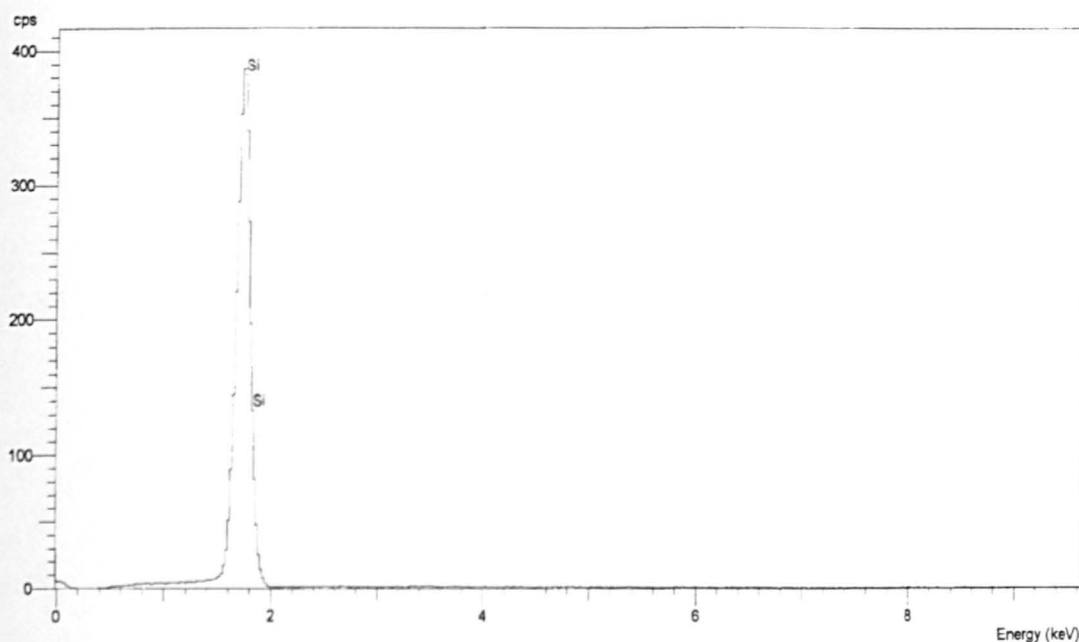


Figure 5-12 EDX Spectrum of Blank area of Silicon Substrate showing only presence of Silicon

5.4.5 Mounting The Particles For AFM.

Mounting On Silicon

A few drops of the sample were dropped on to a square of silicon approximately 5 mm on each side. It was not possible to obtain any results using this method because the particles were pushed out of the way when the tip scanned the surface.

A very thin layer of gold was sputtered on to the surface of the sample. This was enough to hold the particles in place while the tip scanned the surface.

5.4.6 Mounting The Particles For TEM.

Mounting On A Copper Grid.

A copper TEM grid was placed in to an aluminium holder and a few drops of sample were dropped on to the surface of the grid. The solvent washed through the grid, leaving some particles trapped in the grid. This was mounted directly in to the TEM.

5.5 SEM Results and Conclusions

5.5.1 Results From SEM Imaging

SEM Image Of Particles On A Plastic Film Substrate

Figure 5-13 shows a selection of particles on a plastic film substrate. The film and particles have been gold sputtered. The image shows several large $10\text{ }\mu\text{m}$ - $30\text{ }\mu\text{m}$ particles and numerous smaller $1\text{ }\mu\text{m}$ particles on the surface. This is typical of the results found on the SEM images and compares well to the results from particle sizing using laser scattering. The image was taken with an accelerating voltage of 5kV at a magnification of 476 X.

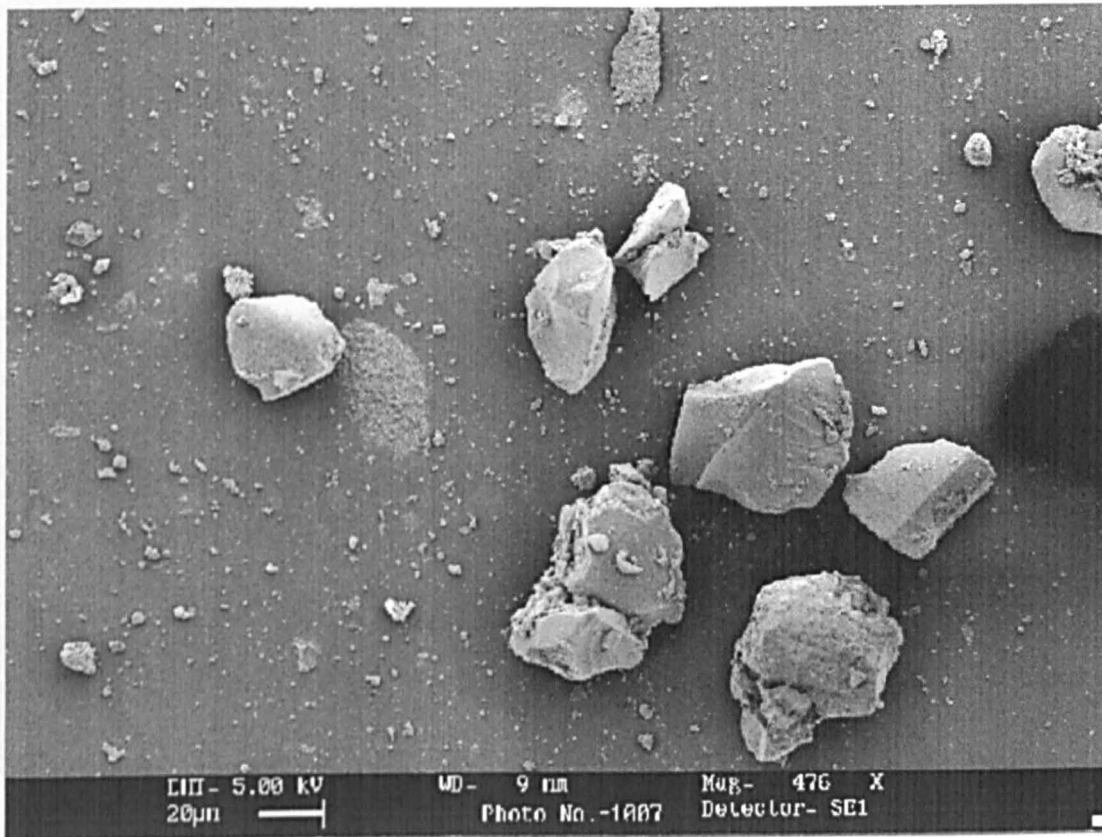


Figure 5-13 Soot Particles on a Transparent Plastic Film Substrate

SEM Images Of Different Particles

Figure 5-14 shows an enlargement of Figure 5-13. The particle on the left shows small (100 nm) flakes on the surface of the particle. This was seen on other particles in the sample, and similar features were just visible on a sample prepared for EDX analysis, although an EDX surface scan was not performed on such a particle.

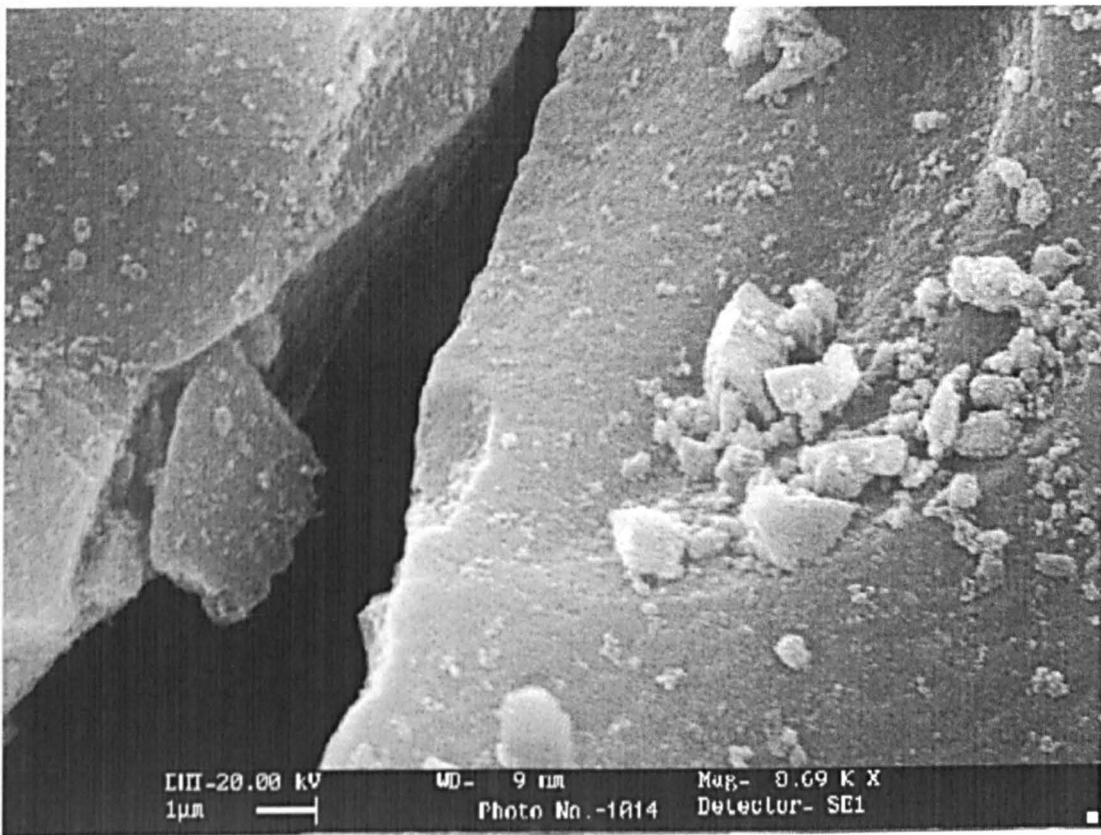


Figure 5-14 Enlarged Section of Previous Image Shows Small Particles and Flakes on Surface of Larger Particles

On the right, a section of a particle can be seen with similar flakes, and also a number of small particles (1 μm or smaller) on the surface. The particles are likely to be carbon.

The two particles shown in Figure 5-15 have a very different appearance, despite coming from the same oil sample and being approximately the same size. Some particles from the oil appear to be large single particles, whereas others are

agglomerations of smaller particles. Section 5.6 shows that the agglomerations are made from chemically different particles.

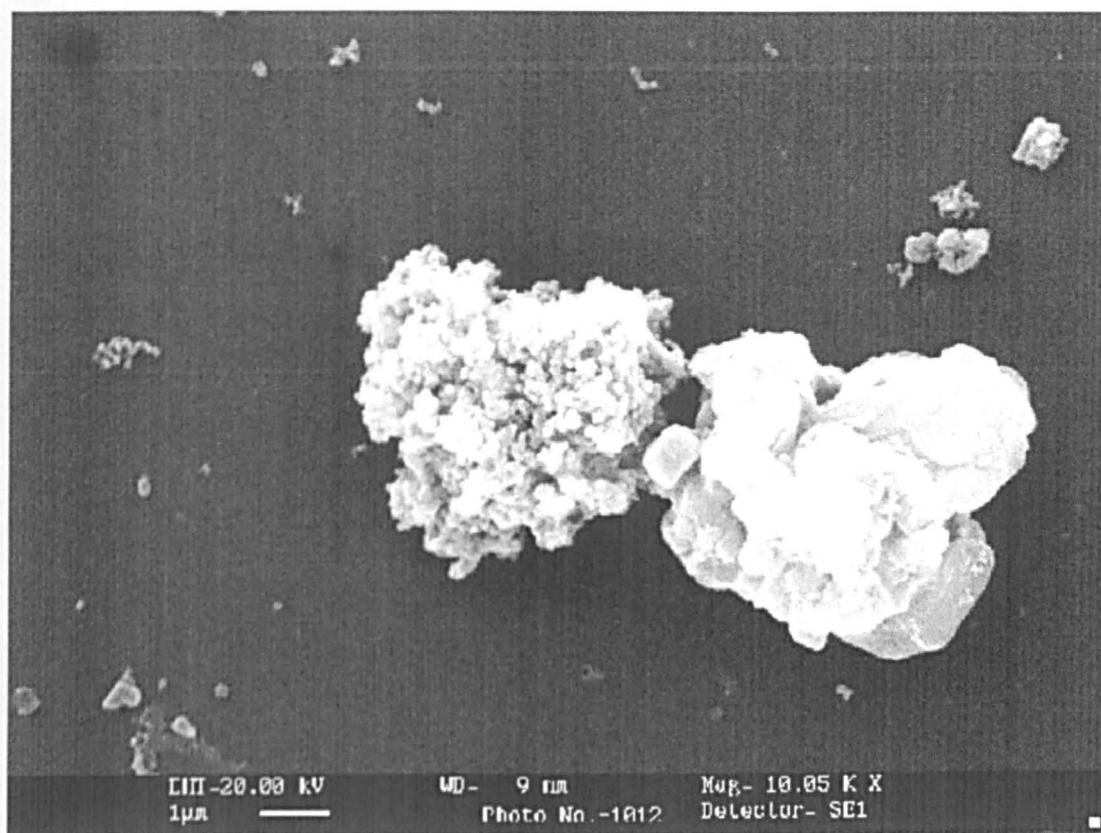


Figure 5-15 Particles Exhibiting Marked Difference in Morphology

Images through a range of magnifications

Images were taken through three orders of magnitude of magnification (Figure 5-16, Figure 5-17 and Figure 5-18), showing that particles over a wide distribution of sizes are present.

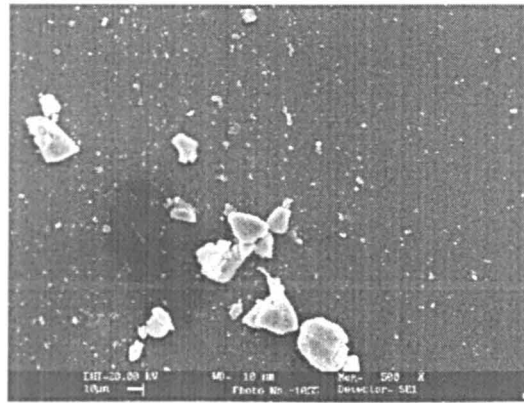


Figure 5-16 1 000 X Magnification

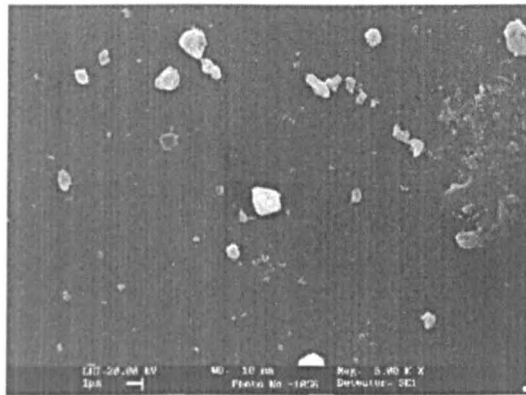


Figure 5-17 10 000 X Magnification



Figure 5-18 100 000 X Magnification

Figure 5-18 suggests the presence of particles smaller than 100 nm. Particles of this size were not identified using laser scattering particle size analysis. AFM results also gave an indication of particles of this size and smaller.

5.5.2 Conclusions from SEM images

Good images of the particles separated from the oil can be obtained using transparent plastic film to remove the particles from the solvent, mounting the film on an aluminium stub and coating with gold. Images of particles down to 100 nm in diameter can be obtained.

The results show that particles can be found over a large distribution of sizes, from 100 nm to 30 μm . in diameter. The larger particles show flakes and small particles as surface detail. EDX analysis gives more information on these surface features. Particles of similar size, which are from the same sample, can have a very different appearance, and some particles are agglomerations of smaller particles.

5.6 EDX Analysis Results and Conclusions

5.6.1 EDX of a Blank Part of the Silicon Wafer

A blank part of the silicon wafer (an area where no particles could be seen on the silicon surface) was selected and an EDX spectrum was obtained for this area. The spectrum is shown in Figure 5-12. The spectrum shows a single large peak for silicon, demonstrating that the silicon surface is a good choice for a substrate for EDX analysis. The peak at zero on the x-axis is to mark the position of zero on the spectrum for calibration.

5.6.2 EDX Of Particles

An image of 3 10 μm particles was obtained on the SEM. One of the particles was selected and the spectrum taken. The particle appeared to be an agglomeration of smaller particles as seen on the SEM image. The spectrum clearly shows oxygen and calcium, with smaller peaks for sodium, sulphur and chlorine and is shown in Figure 5-19.

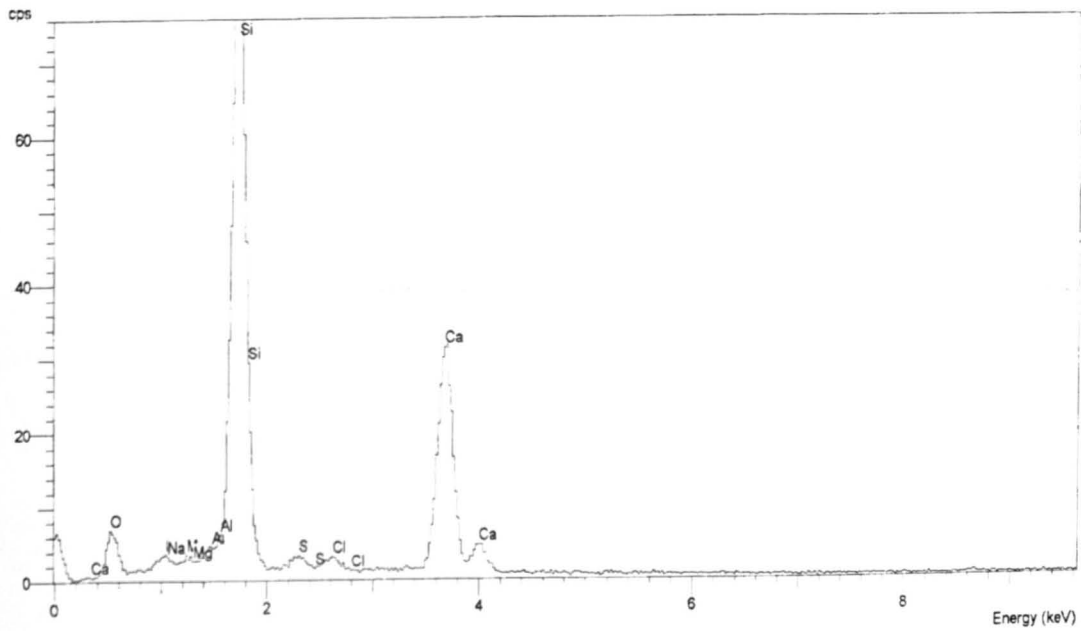


Figure 5-19 EDX Spectrum of large 10µm Particle. Clear Ca and O Peaks. Discernible Na, S and Cl Peaks.

The enlarged spectrum shown in Figure 5-20 shows peaks for magnesium zinc and aluminium.

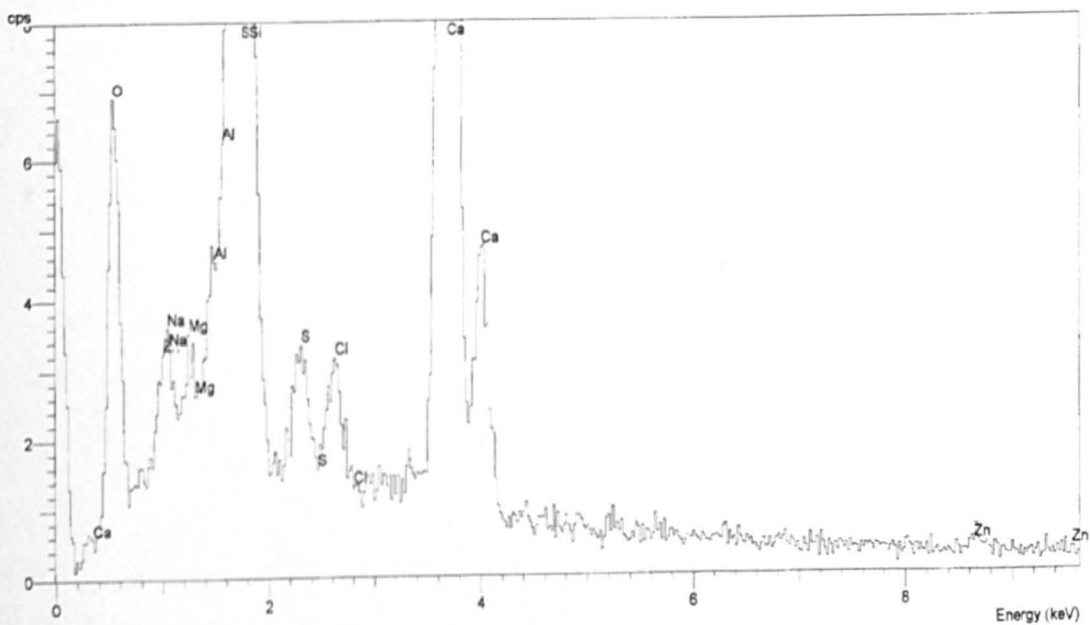


Figure 5-20 Magnification of previous Figure showing peaks for Mg, Zn and Al.

Figure 5-21 shows the spectrum of a similarly sized (10 μm) particle from the same SEM image, but shows a very different spectrum from that seen in Figure 5-19. The spectrum shows peaks for iron, aluminium and potassium.

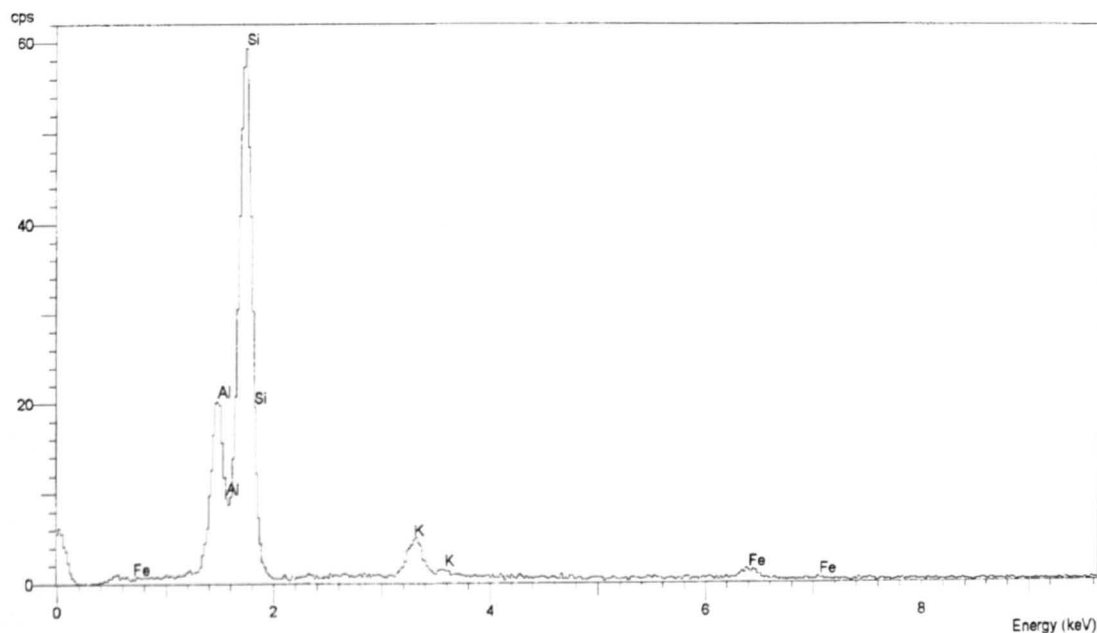


Figure 5-21 Spectrum from Similarly Sized Particle But Showing Al, K and Fe.

A 30 μm particle made from an agglomeration of smaller particles was selected, which was zoomed to fill the entire image and a single crystal was selected for the EDX scan. The spectrum in Figure 5-22 shows that the crystal is predominately calcium, with a small peak for oxygen.

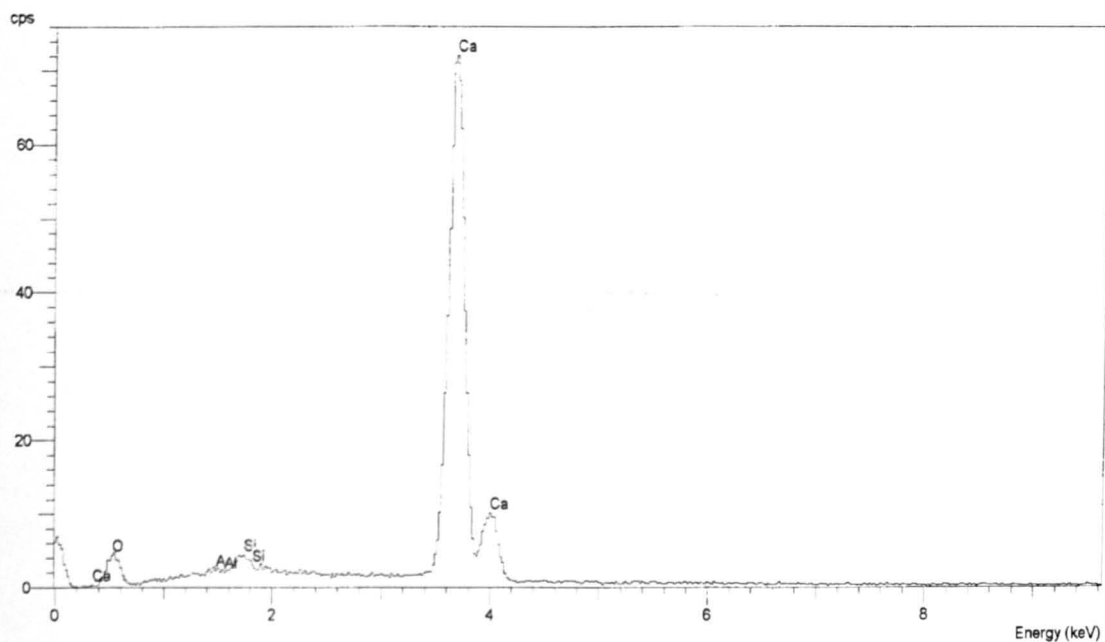


Figure 5-22 EDX Spectrum of Particle Surface. SEM Image Was Magnified To Produce Larger Target Area for EDX To Minimise Si Peak

A zoomed scan of a second particle shows oxygen, aluminium, potassium and iron. This is shown in Figure 5-23.

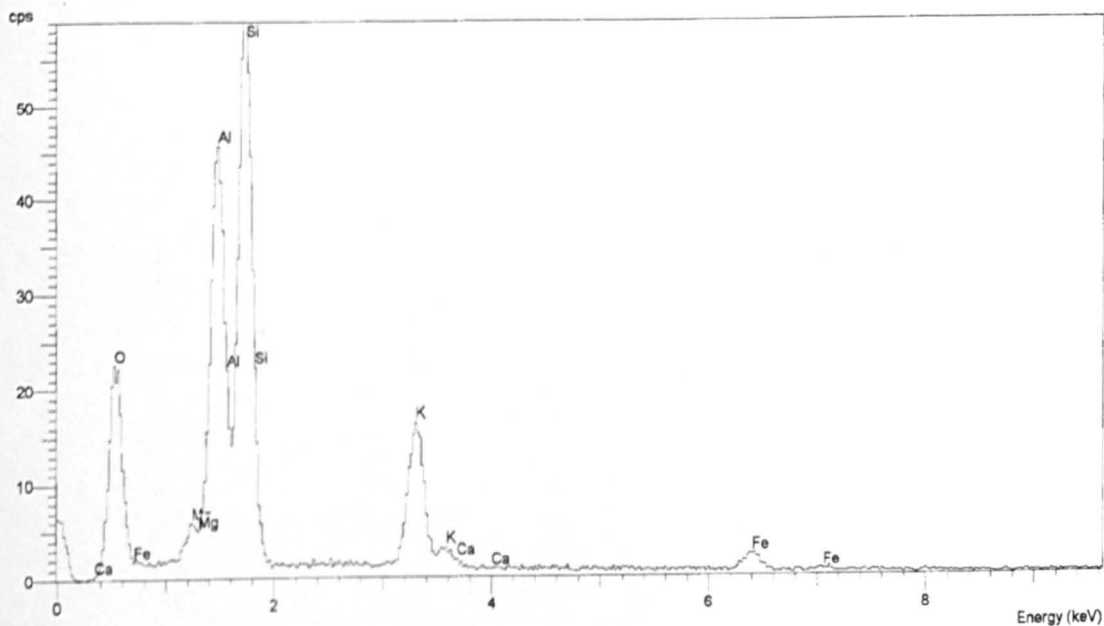


Figure 5-23 EDX Spectrum of Area of Surface of Second Particle Showing Different Elements

Scans of other particles suggest that each particle is either made up from predominately calcium and oxygen, or aluminium, potassium, iron and oxygen.

5.6.3 EDX Particle Surface Scans

The EDX can be set to scan over the surface of an entire image and record the number of x-rays detected from each part of the image for specific energies. A spectrum of a chosen particle was obtained from a line scan across the particle and the energies of the most prominent peaks were used to set the EDX scan. The EDX will then record the position in the image for each detected x-ray at these selected energies.

A particle, approximately $50\text{ }\mu\text{m}$ x $20\text{ }\mu\text{m}$ was found on the SEM and the magnification set to fill the image with the particle. The line spectrum indicated that O, Al, S and Ca were present and peaks with these energies were selected for the EDX as well as Si for the substrate. A surface map of the image for these energies was then taken with the EDX. The results are shown below in Figure 5-25, Figure 5-26, Figure 5-27, Figure 5-28 and Figure 5-29.

The images were created by taking the .tif files generated on the EDX computer and using software to combine them with the base image. The EDX gives a black image, with areas becoming progressively lighter where more x-rays are detected at any particular point. Computer software (Paint Shop Pro) was used to create a negative image and turn it from a grey scale image to a colour image. Areas where x-rays of the correct energy are detected are now shown as colour on the image. This map was then merged with the base image using Aldus Photostyler. To create the map of aluminium and calcium, the aluminium map was simply merged with the already merged image of calcium and the base image.

Figure 5-24 shows a low resolution image of the particle at all energies for comparison to the EDX results. Figure 5-25, Figure 5-26 and Figure 5-27 show the maps for Ca, Al and O respectively as colours overlaid on to the base image. Figure 5-29 shows the maps of Al and Ca overlaid as different colours on to the base image.

From the base image in Figure 5-24, the particle appears to be made from several smaller particles, each approximately $1\text{ }\mu\text{m}$ in diameter. The EDX results show that the different particles making up the large particle are made from different elements.

Crystals can be seen that clearly have a high calcium content and other areas of the particle are made from aluminium, but there are very few areas made of both calcium and aluminium.

The areas of oxygen, Figure 5-27, closely match the areas of aluminium, suggesting that the surface of the aluminium is oxidised. In practice, this is likely, because the sample was made several days before the EDX results were taken and aluminium oxidises quickly. Further tests could be made to see if the aluminium particles from similar oil samples are, in reality, oxidised by taking fresh samples from the engine and then separating and mounting the particles before they had time to oxidise. Tests could also be made to see if the aluminium oxidises while it is still in the oil.

The map of S (Figure 5-28) shows no localisation on the particle, showing that any sulphur present is scattered throughout the sample. In reality, any sulphur energies recorded may have been lost in the background noise because of the small size of the peak. Hence, the sulphur map may just be showing a random scatter of background noise.

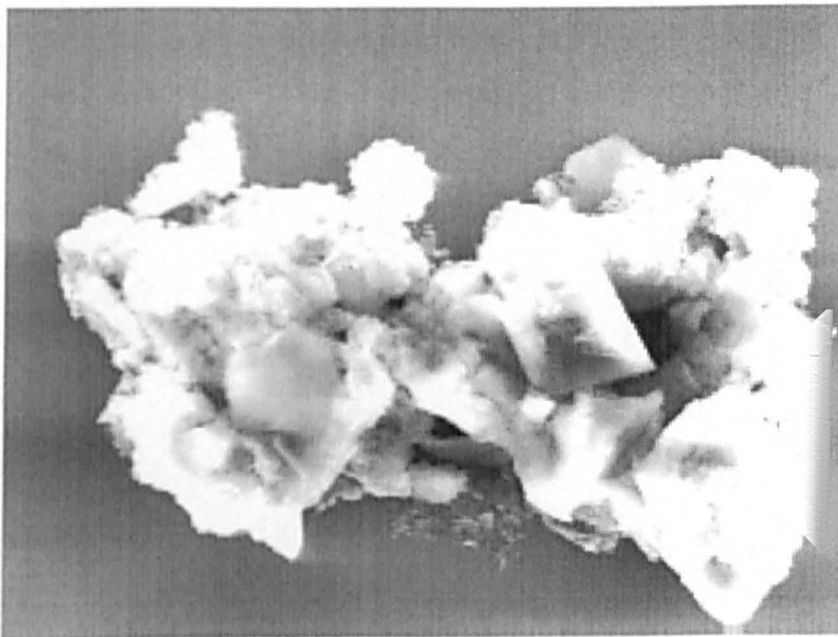


Figure 5-24 Agglomerated Particles

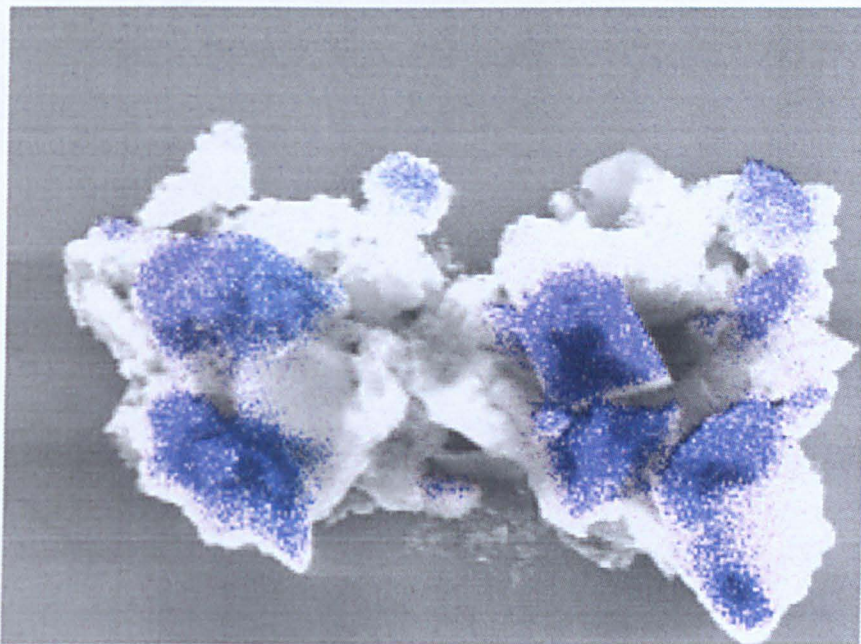


Figure 5-25 Areas on Surface of Ca Shown in Blue

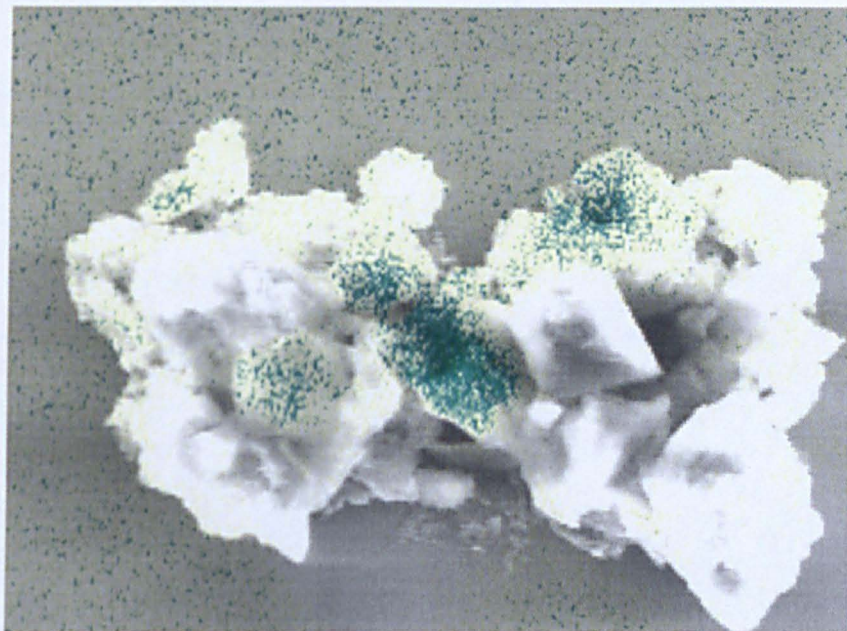


Figure 5-26 Areas on Surface of Al Shown in Green

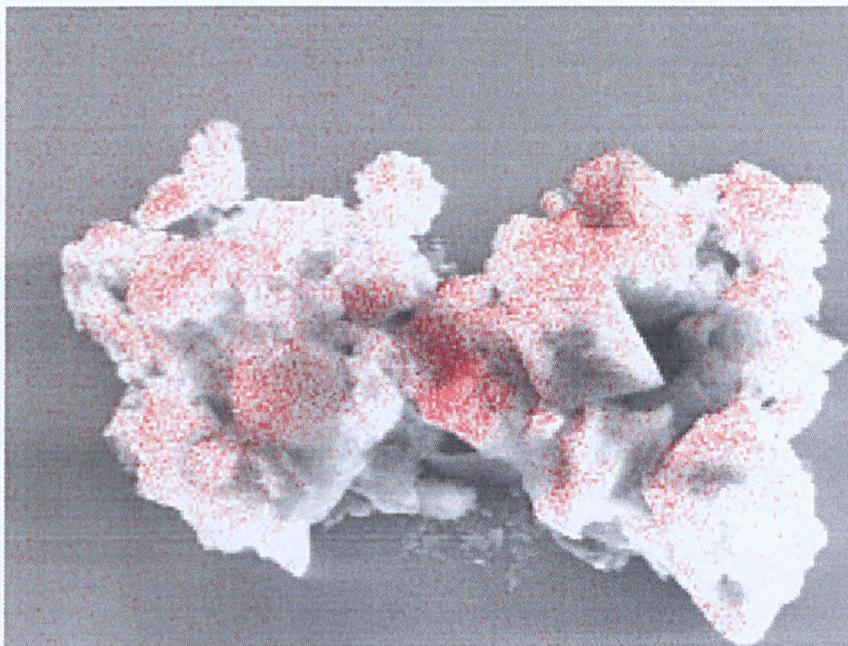


Figure 5-27 Areas on Surface of O Shown in Red

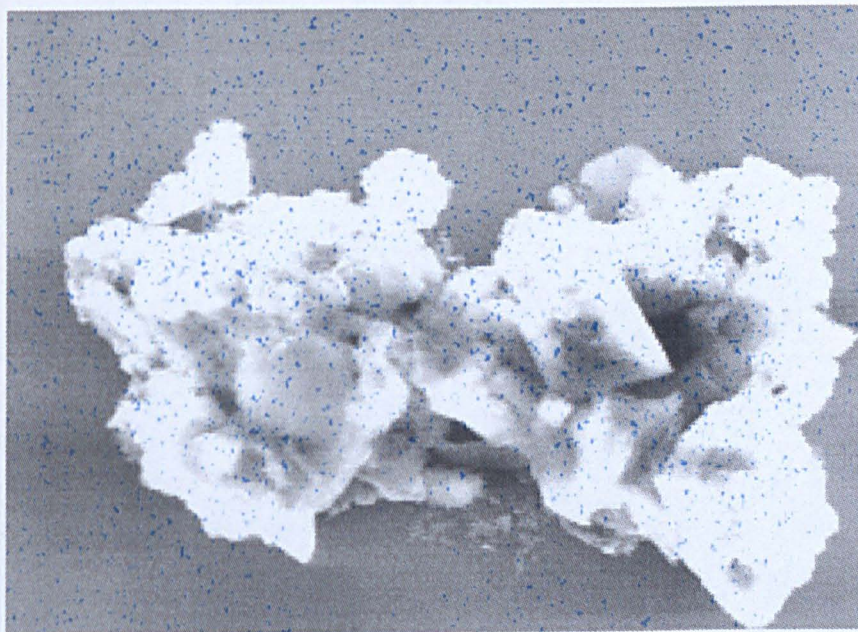


Figure 5-28 Areas on Surface of S Shown in Pale Blue

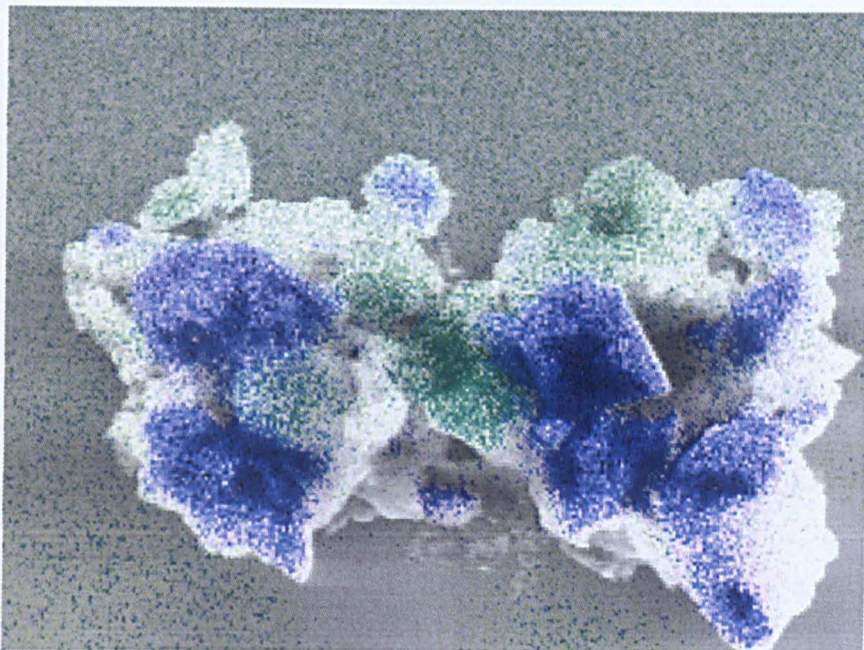


Figure 5-29 Areas on Surface of Ca (Blue) and Al (Green).

5.6.4 EDX Concentration Maps

Figure 5-30, Figure 5-31 and Figure 5-32 show maps of the concentrations of oxygen, aluminium and calcium respectively. The areas of yellow have the greatest concentration, with the concentration reducing through red, purple, blue, pale blue and green as the lowest concentration. White areas have no recorded x-rays at that energy. Again, the maps show localised regions of calcium and aluminium, which compare to the maps shown in Figure 5-25, Figure 5-26 and Figure 5-27.

Figure 5-31 shows the concentration of aluminium in the particle. The light green background suggests a concentration of aluminium but is in fact silicon as their EDX energy peaks overlap. White patches where neither silicon nor aluminium are observed.

It should be noted that the colours representing concentration are not calibrated between each map, and the maps are in effect normalised to a maximum concentration for each individual map, represented in yellow. The levels of concentration do not

given quantitative values and are intended only as an indication of the levels of concentration over the surface.

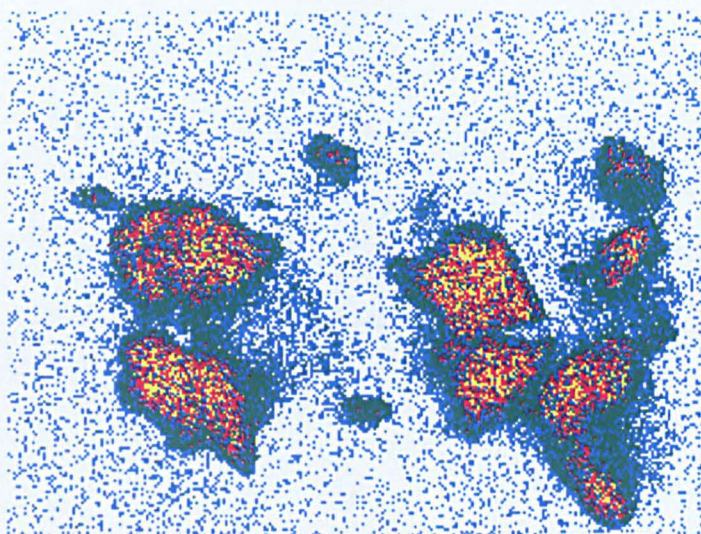


Figure 5-30 Concentration Map of Ca on the Particle

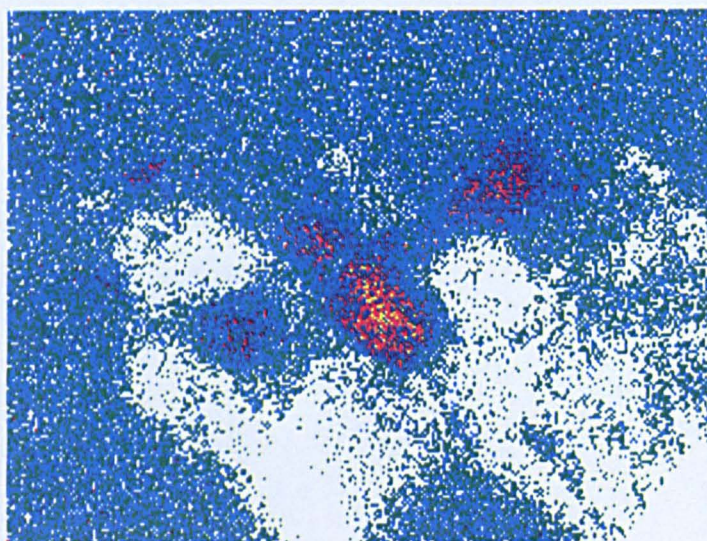


Figure 5-31 Concentration Map of Al on the Particle

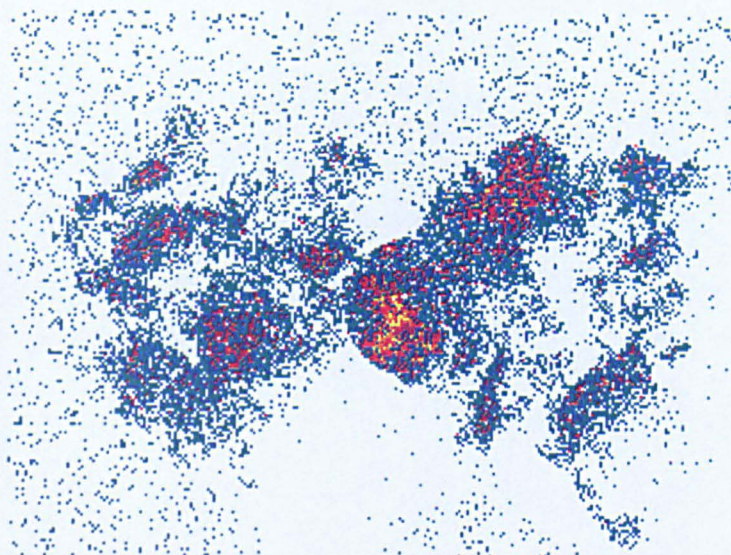


Figure 5-32 Concentration Map of O on the Particle.

5.6.5 Conclusions From EDX Analysis

EDX is a useful method for obtaining an analysis of the elements on the surface of the particles. Silicon makes a suitable substrate because of its purity, and the problems with charging found with using silicon as a substrate for imaging are not as limiting with EDX because the image quality does not need to be as high. Individual particles can be selected and the spectrum of that particle can be taken. Agglomerations of particles can also be scanned and individual particles from the agglomeration can be selected and the spectrum obtained if a good enough image can be obtained on the SEM.

Surface scans of particles are possible and give very good results. A higher image quality is needed for a surface scan to obtain a fine resolution, and this becomes more difficult for smaller particles because of problems with charging on the silicon substrate, but excellent results can be obtained from particles greater than $1\text{ }\mu\text{m}$. Surface scans of agglomerates clearly show the differences in the constituent particles in the agglomeration. The concentrations of elements on the surface can also be obtained using image processing software.

Individual particles consisted of calcium and oxygen or aluminium, potassium, iron and oxygen, although a thorough analysis of many particles is needed before any conclusions about the physical nature of the particles can be made.

5.7 AFM Results and Conclusions

5.7.1 Images Of Particles At Different Magnifications

The following images were taken using the atomic force microscope. The images were taken over a range of magnifications. The number written above each image is the length of one of the sides of the (square) image.

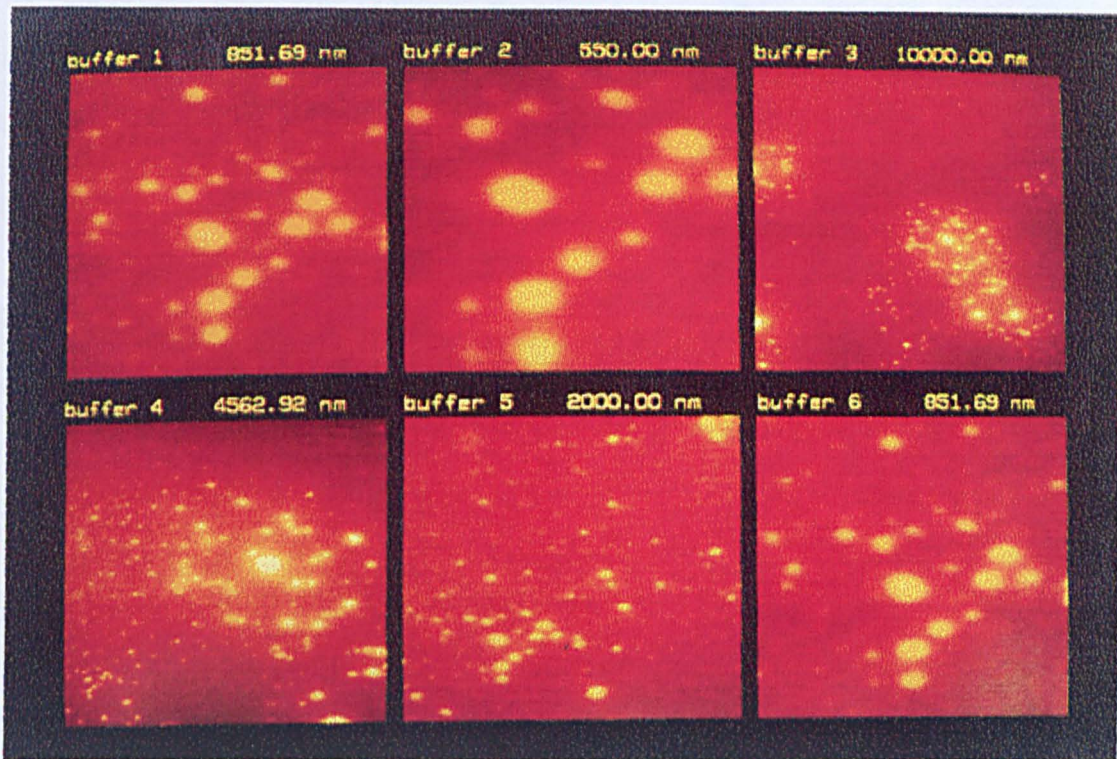


Figure 5-33 AFM Images of Soot Particles on a Silicon Substrate Over a Series of Magnifications

The surface features seen are probably soot particles from the oil sample. The clean surface of the silicon wafer was imaged, and revealed no surface features, appearing very flat. The surface features were seen after a drop of solvent containing carbon particles was dropped on to the surface and gold coated. The objects seen in the images are larger than the size of the particles of gold, which the sputtering process deposits (< 10 nm), so it looks probable that they are from the oil sample.

5.7.2 3D Image Of The Particles And Tip Convolution.

Figure 5-34 shows a 3D projection of the silicon surface, showing surface features measuring tens of nanometers in diameter. The objects appear as peaks on the surface of the substrate rather than spherical particles. The reason for this can be understood by looking at how the tip scans over the surface of the sample.

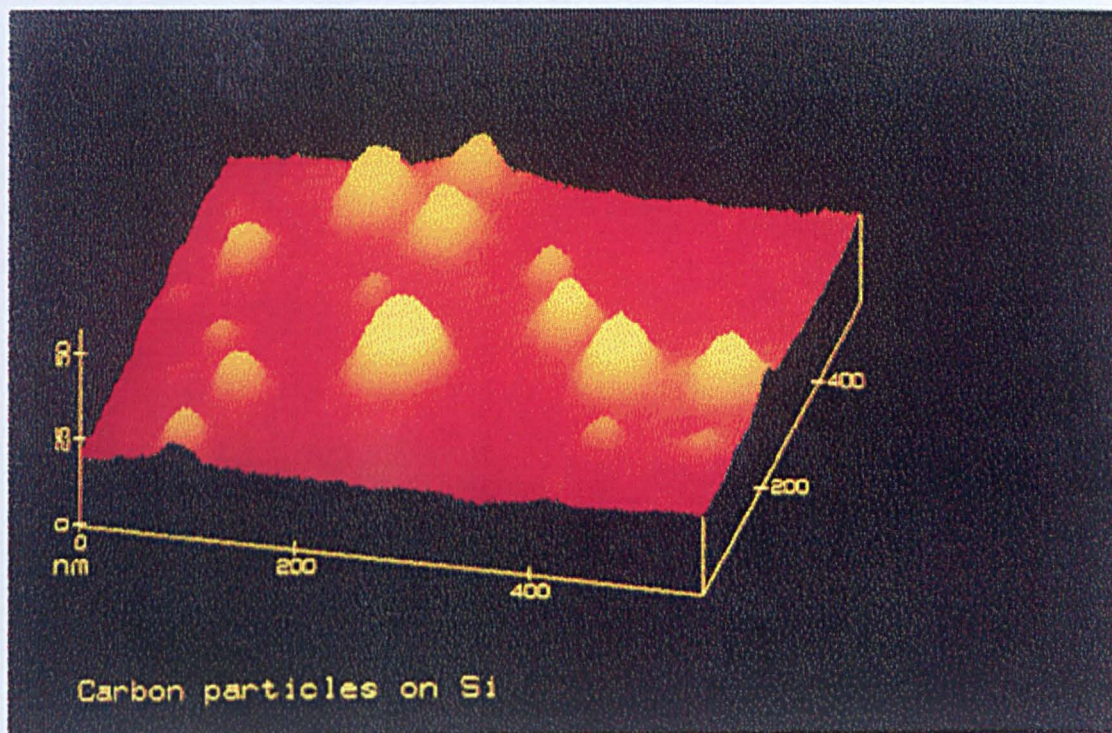


Figure 5-34 3D Projection of the Silicon Surface. Observe Features 10's of Nanometers in Diameter

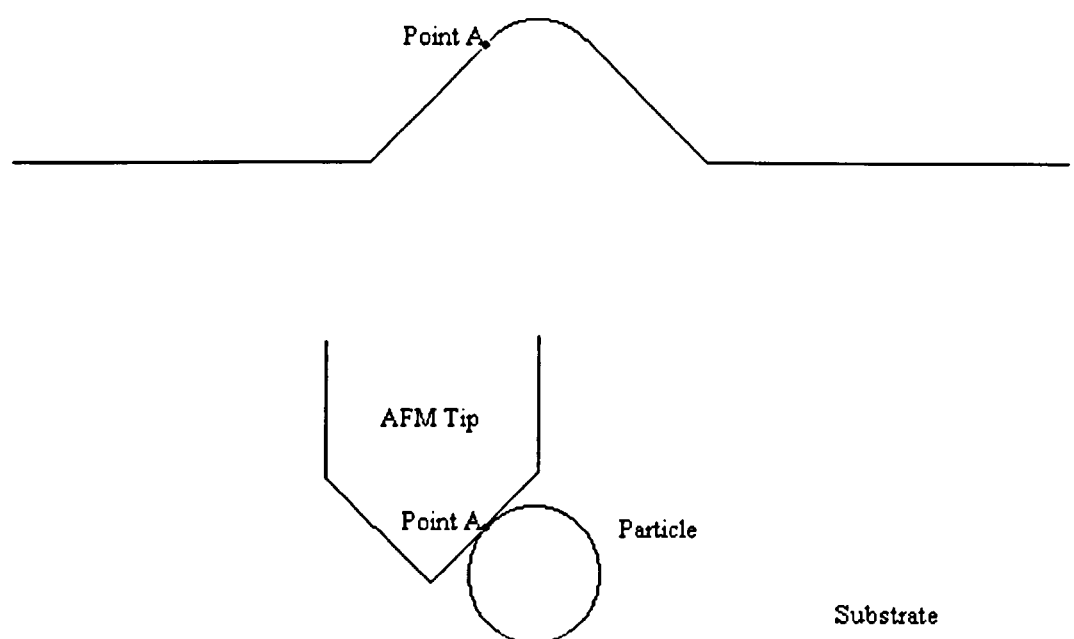


Figure 5-35 Representation of Tip Convolution Error. Tip is of Comparable Size to Particle

When the edge of the tip reaches the edge of a particle, it begins to rise as it moves over the particle. The end of the tip is not actually in contact with the particle until it reaches point 'A'. Before this point, the height of the tip varies according to the angle of the point at the end of the tip. After point A, the tip follows the surface of the particle correctly. Similarly, the tip will follow its slope at the other side of the particle. While the end of the tip is not in contact with the sample, the AFM is only giving information on the tip, and not on the particle. The AFM will only give information on the particle when the end of the tip is actually touching its surface. This is further demonstrated in Figure 5-36.

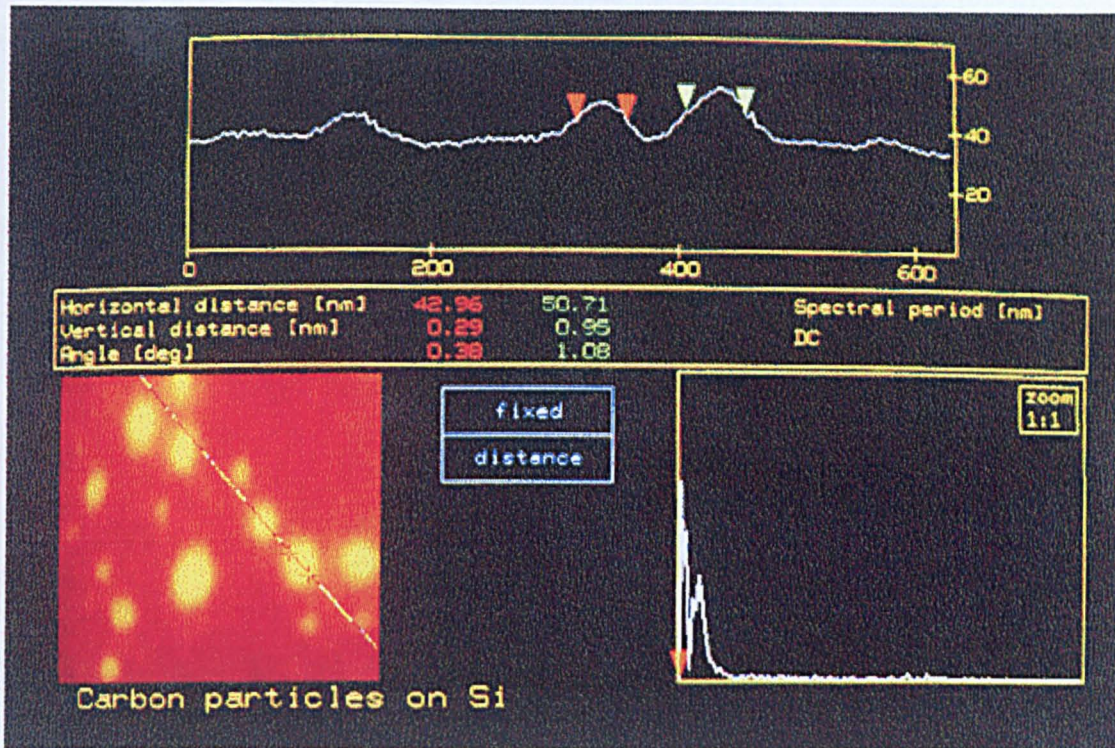


Figure 5-36 Height of X-Section through Image Shows Larger Particles Approx. 20nm diameter

This shows a cross section through the data taken from the AFM. The green and red markers indicate a size of 40 nm to 50 nm. This is in fact larger than the actual diameter for the reasons described. The height of the particles gives a much better indication of their true size. The y axis, which is calibrated in nanometers shows that some of the larger particles are approximately 20 nm in diameter.. This is further evidence to suggest the existence of sub 100nm particles, which were indicated by SEM. Particles smaller than 20 nm, should not be considered as definitely being from the sample because these sizes approach the size of the gold grains deposited by sputtering.

- ¹ Malvern Mastersizer S User Manual
- ² In-house method to determine soot content by TGA - Detroit Diesel
- ³ Seifert, Measurement of Soot in Diesel Engine Lubricating Oil, *SAE* 951023.
- ⁴ Kittleson, D. et al, Size Distribution of Diesel Soot in the Lubricating Oil, *SAE* 912344
- ⁵ Colacicco, P. et al, The Role of Soot Aggregation on the lubrication of Diesel Engines, *Trib. Trans.*, 38, No.4 pp959-965, 1995.
- ⁶ Gautam, M. et al, Contribution of Soot Contaminated Oils to Wear, *SAE*981406
- ⁷ Kawamura, M. et al, Electronic Microscopic Observations of Soots in Used Diesel Engine Oils, *Lub. Eng.* July 1987
- ⁸ Sato, H., Study on Wear Mechanism by Soot Contaminated in Engine Oil (First Report: Relation Between Characteristics of Used Oil and Wear), *SAE* 1999-01-3573
- ⁹ Mainwaring, R., Soot and Wear in Heavy Duty Diesel Engines, *SAE*971631

6 Final Discussion and Conclusions.

6.1 Final Discussion

The Blotter Spotter work showed that the succinimide dispersant used in the 57a/b/c and 58a/b/c oil series did not appear to be successful in the piston ring zone. The high temperatures in this zone preclude proper function of the dispersant, leaving any dispersancy action down to the detergent additive in the formulation. The mixed salicylate detergent additive was better than the phenate/sulphonate detergent additive in this respect. The particle size analysis results similarly demonstrated that the dispersant has very little impact on particulate control in the piston ring zone, especially in the results from the first matrix of oils. However the conclusion from the detergent is different, that the phenate/sulphonate, rather than the mixed salicylate detergent showed better results. The Blotter Spotter test determines an oils ability to disperse insolubles over a silica plate, whereas the particle size analysis determines the oils ability to resist particle agglomeration. Both of these properties are related to the dispersancy of the oil.

In the blotter spotter test, the few large particle agglomerations might not be dispersed very far, probably not to the limit of the particulate front in the oil spot, whereas the much larger number of much smaller $\sim 0.8\mu\text{m}$ particles would. As such, the method only measures the oils ability to disperse small particulate. The particle size analysis technique is much more sensitive to particulate agglomerations and so this technique can further the information on an oils dispersancy.

In interpreting the particle size analysis results, however, agglomerations cause problems with the interpretation of the trends seen in the $\sim 0.8\mu\text{m}$ size band making it difficult to compare oils of different formulations. Changing this method to use the number of particles rather than the % in volume would enable better interpretation and particle size analysis would then be able to replace the function of the blotter spotter test. The blotter spotter test is a very rapid and cheap method, but it is limited in it's ability to characterize all aspects of top ring zone oil dispersancy. At the moment, used in conjunction, the two methods can fulfil this role.

Although the Blotter Spotter work was not carried out on the second matrix of oils, with its dispersant selected for improved diesel engine performance, the particle size analysis showed an improvement in the dispersancy performance, at least by showing that the treat rate of the dispersant now had a discernible effect that was not evident from the particle size analysis of the first matrix of oil samples.

Both the Blotter Spotter and Particle Size analysis results demonstrated that dispersancy and particulate control are superior in the sump region with any of the additive systems tested. This region of the engine is much cooler than in the ring zone and has a larger volume of oil with available dispersant for dispersion of solids.

Blotter Spotter and Particle Size Analysis work demonstrated that both of these techniques are not really suitable for studying particulates and dispersancy in oil samples derived from the piston ring zone of a gasoline engine.

The morphology studies showed successful methods for the preparation of particulate from used oil samples for use with SEM and EDX for qualitative studies. The examination of a phenate / sulphonate based detergent pack lubricating oil from the top ring zone (with zero dispersant – chosen because the particle size analysis results showed the two most distinct particle size bands and the clear crossover of 0.8 μ m to 8-12 μ m agglomerations) showed particles of the following size ranges; sub-micron particles (observed by SEM and confirmed by AFM), \sim 1 μ m and $>$ 10 μ m.

Much of the SEM/EDX work centred on development of those techniques for analysis of used diesel oil samples finding that for SEM the best substrate for the particles was in fact transparent plastic film followed by gold sputtering to eliminate the charging that would be seen from the plastic substrate. For the SEM/EDX then the gold sputtering was not to be used. Mounting the particles on silicon wafer was the preferred solution as the silicon is very pure and although charging of the silicon wafer does take place, the image quality is sufficient for EDX.

The SEM images confirmed the presence of the larger aggregations seen with the particle size analysis. Distinct types of particles were seen. Those smaller

agglomerations aggregations that can be attributed to soot and the very much larger, crystalline structure that warranted further investigation by EDX. The EDX analysis of this type of particle showed it to mainly consist of calcium, oxygen, sulphur and aluminium. The aluminium likely to be soluble wear element, while the other main constituents are likely to be sulphates of calcium and originate from the detergent portion of the additive package.

The dispersant and detergents seem to form a synergy with each other and certain types of dispersants might be more effective with some detergents and at specific treat rates. The combination of the Improved Blotter Spotter and the Laser Scattering Particle Size Analysis techniques as applied to piston ring zone oil samples could be used as a generic screening test for dispersant/detergent additive effectiveness in the piston ring zone. Combining this further with morphology studies such as the SEM/EDX method described here can also yield details of the agglomerations and aggregations produced when particulate control in the piston ring zone is seen to be out of control.

The old ring pack designs of the diesel engine used in this study, as previously mentioned, with no low emissions criteria to fulfil, has a relatively high lubricant replenishment rate through the ring pack of relatively fresh sump oil. A more modern low emission engine would not replenish the ring zone oil as quickly and would subject the detergent/dispersant package of the oil to a greater ring zone residence time, stressing the oil further. The sump oil, especially in a modern diesel engine would be expected to contain a great deal more soot, at up to 5% by weight. This already sooty oil for ring zone replenishment and higher residence time in the ring zone might show a decreasing dispersancy performance over time in the piston ring zone of a modern low emission diesel engine. Any dispersancy / particulate control studies or screening tests would be better served with the use of a more modern diesel engine with a flying tube piston ring zone sampling system applied.

The particulate size ranges observed from the Laser Scattering Particle Size Analysis, the SEM and AFM gave results that were in agreement with the literature. Some researchers also use SEM or TEM for generic particle size distribution analysis, using image analysis techniques to determine size distributions. It is an expensive method and

can easily be replaced by the much cheaper and very much more rapid laser scattering particle size analysis method. Recently, optional units have become available on laser scattering particle size instruments that can determine particle sizes down to $0.05\mu\text{m}$, within the region of primary particulate sizes, before the first agglomeration takes place. This also further strengthens the case to use against the use of SEM/TEM and towards the use of Laser Scattering Particle Size analysis but also now negates the need to use the AFM for studying primary particulates.

6.2 Conclusion

In reference to the original objectives stated in Chapter 1, TRZ sampling was successfully used in the Petter AA1 and W1 engines and on the two matrices of engine oil formulations and the samples generated for the purposes of the analytical study, which followed.

The Blotter Spotter Technique was successfully developed and improved for the study of remaining useful dispersancy of the above degraded lubricants from the piston ring zone finding that:

- Full dispersant treat not better than half dispersant treat in TRZ in either gasoline or diesel engine
- Full dispersant treat better than half dispersant treat in sump of diesel engine
- Mixed salicylate detergent acts with dispersant performance in the TRZ of gasoline and petrol engines
- Succinimide dispersant is overall, not effective in the TRZ of diesel or gasoline engines in terms of dispersancy described by the blotter spotter test

The laser scattering particle size analysis technique was also successfully developed to investigate the particle size distributions of the above degraded lubricants from the piston ring zone finding:

- Direct evidence of particle agglomeration and aggregation and breakdown of dispersant control in the piston ring zone
- The phenate/sulphonate additive formulations performed better in the TRZ than the salicylate formulations in terms of control of particulate growth
- The high molecular weight thermal succinimide dispersant is less effective than the lower molecular weight variant of the same dispersant in terms of control of particulate growth in the TRZ
- Overall the dispersant performs poorly in the TRZ but can be influenced by dispersant type

Electron Microscopy techniques were developed and applied to the study of used TRZ oil samples. The SEM work concluded:

- Plastic OHP transparency film was the best substrate for SEM images after the particulate had been applied and the sample gold sputtered
- Three distinct types of particulate observed. Small singular or small agglomerations of carbon. Larger aggregates of carbon and much larger crystalline structures, subsequently studied by EDX

The EDX analysis technique was developed and concluded:

- Silicon wafer was the best substrate for insoluble oil particles for SEM/EDX analysis
- Analysis of a crystalline structure showed the particle to primarily consist of Ca, S, O and Al. This type of large particle is probably a sulphate of calcium and originates from the detergent portion of the additive package. The Al formed from wear particulate
- EDX surface scans and image manipulation showed that the Ca and Al occupy distinctly different areas of the particulate studied

AFM was developed for the study of soot particulates and confirmed the presence of primary unagglomerated particles of soot.

In conclusion, this thesis has shown that the two succinimide type dispersants tested do not perform adequately in the piston ring zone, but do perform in the sump. The detergent additives perform the role of dispersant in the piston ring zone.

6.3 Recommendations

Blotter Spotter

In order of priority

- Further development of the method, especially improving spot application with accurate automated liquid handlers or automated TLC spotters
- A comparison of dispersant types, especially succinimide dispersants of different molecular weights
- Comparisons of dispersant performance with respect to engine load and speed
- Investigations of other additive-dispersant interactions and impact on TRZ and sump dispersancy performance such as interactions between ZnDTP-dispersant and friction modifier-dispersant

With a suitably designed and statistically driven experiment, there is scope to transpose this method into a measure of remaining useful dispersancy of diesel engine oils. This can be applied to top ring zone oil samples or as a general engine test or field method for sump samples.

Particle Size Analysis

In order of priority

- Representing the particle size distributions in terms of relative number of particles in a size band over time rather than volume%. This would remove the ambiguities that arise with using volume% where other very large agglomerations exist.
- Different detergent / dispersant package chemistries and the effect other additive - additive interactions and their effect on dispersancy in the piston ring zone.
- Taking into account engine running parameters with the particle size results and using multivariate analysis techniques may help to elucidate further trends in particulate agglomerations.
- Development of technique to include gasoline engine oil derived samples. Could be achieved by removal of particulate from the bulk sample by centrifuge, dissolving

the oil in a solvent, centrifuge, decant, further solvent dilution, centrifuge etc. There would probably only be enough in a sump sample to achieve enough particulate to introduce to the Mastersizer. Another possibility is development of a thin film cell with no solvent dilution.

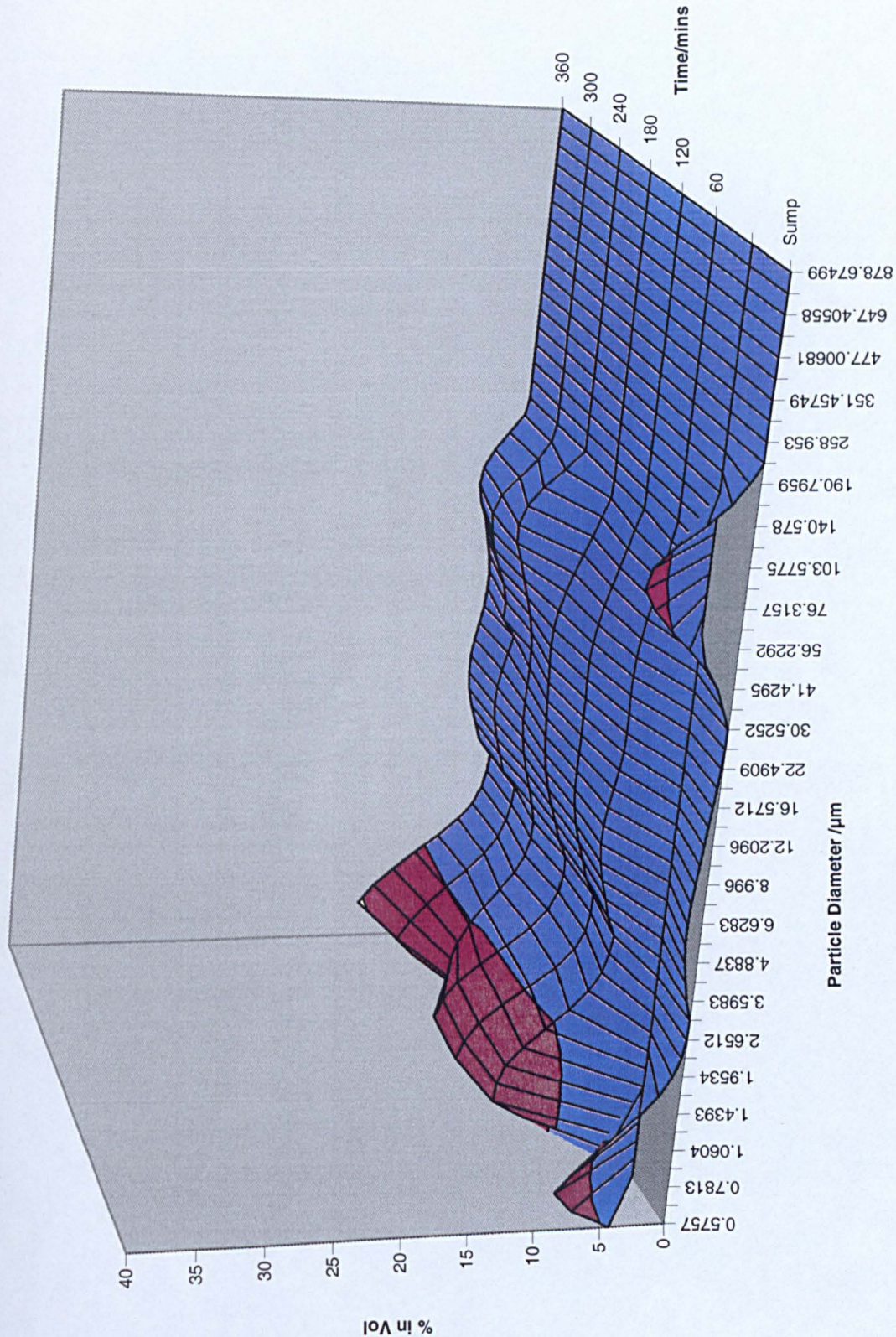
Studies of Particulate Morphology in the TRZ

In order of priority

- SEM/EDX on a larger sample of particulates to further elucidate types of particulates found in the TRZ
- Application of the TRZ sample and SEM/EDX technique to study the changes in particulate morphology throughout the engine run
- Vary the types of dispersant and detergent packages used in the original oil samples to examine how additive systems influence the particulate morphology

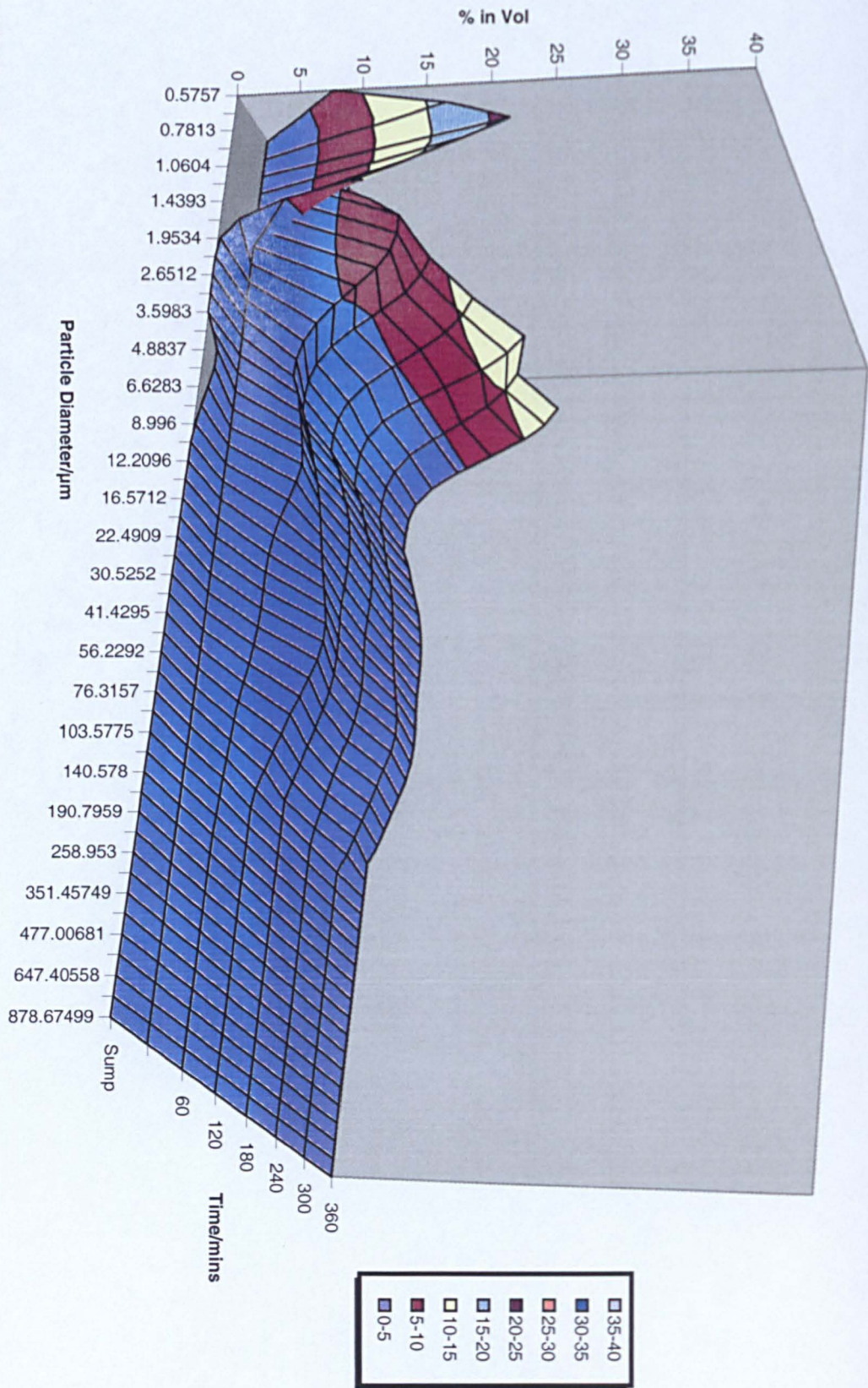
Appendix 1 – Particle Size Contour Plots for Petter W1

Particle Size Distribution for ATL953/057a/01
W1 TRZ 60-360mins



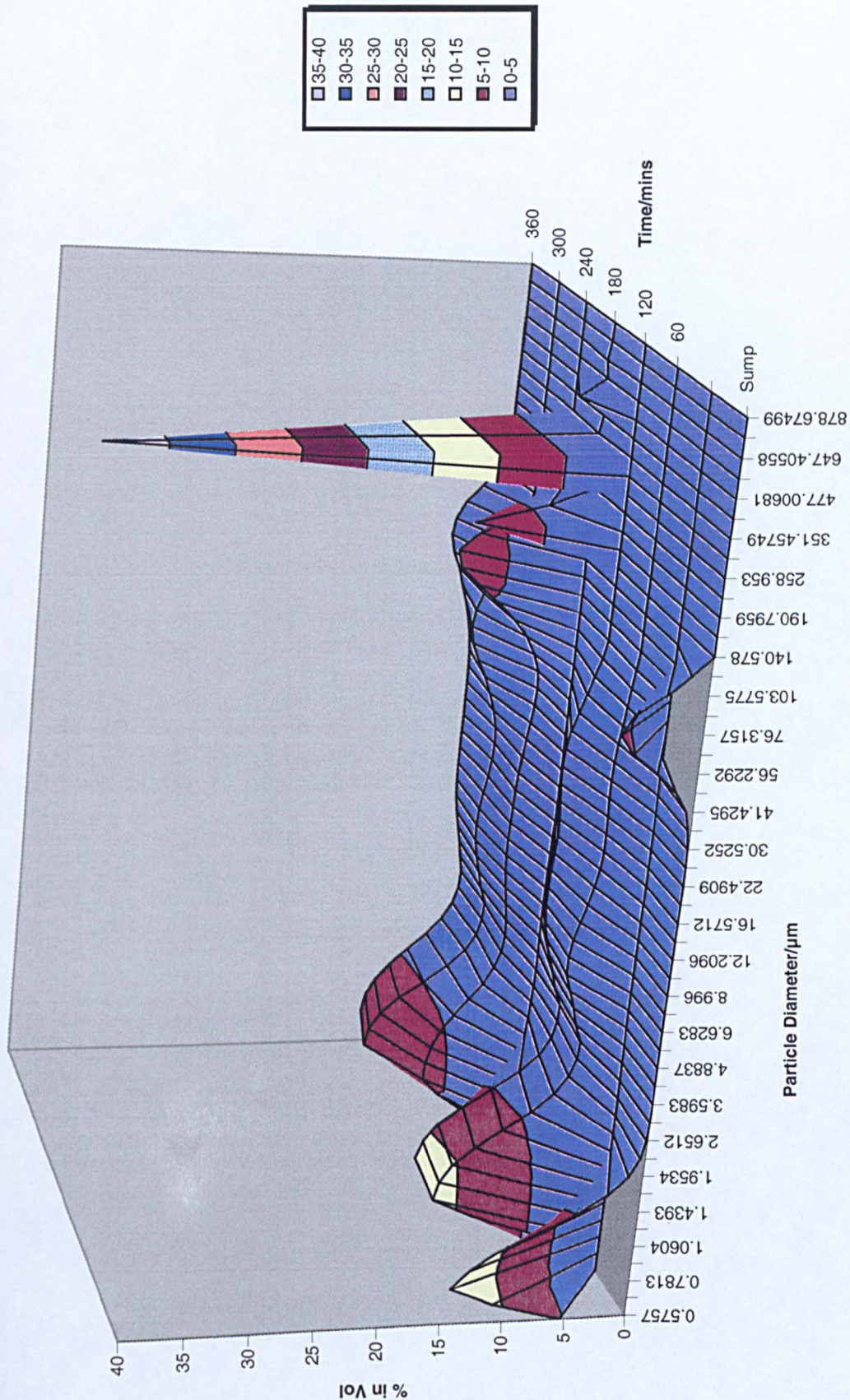
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/057b/02
W1 TRZ 60-360mins



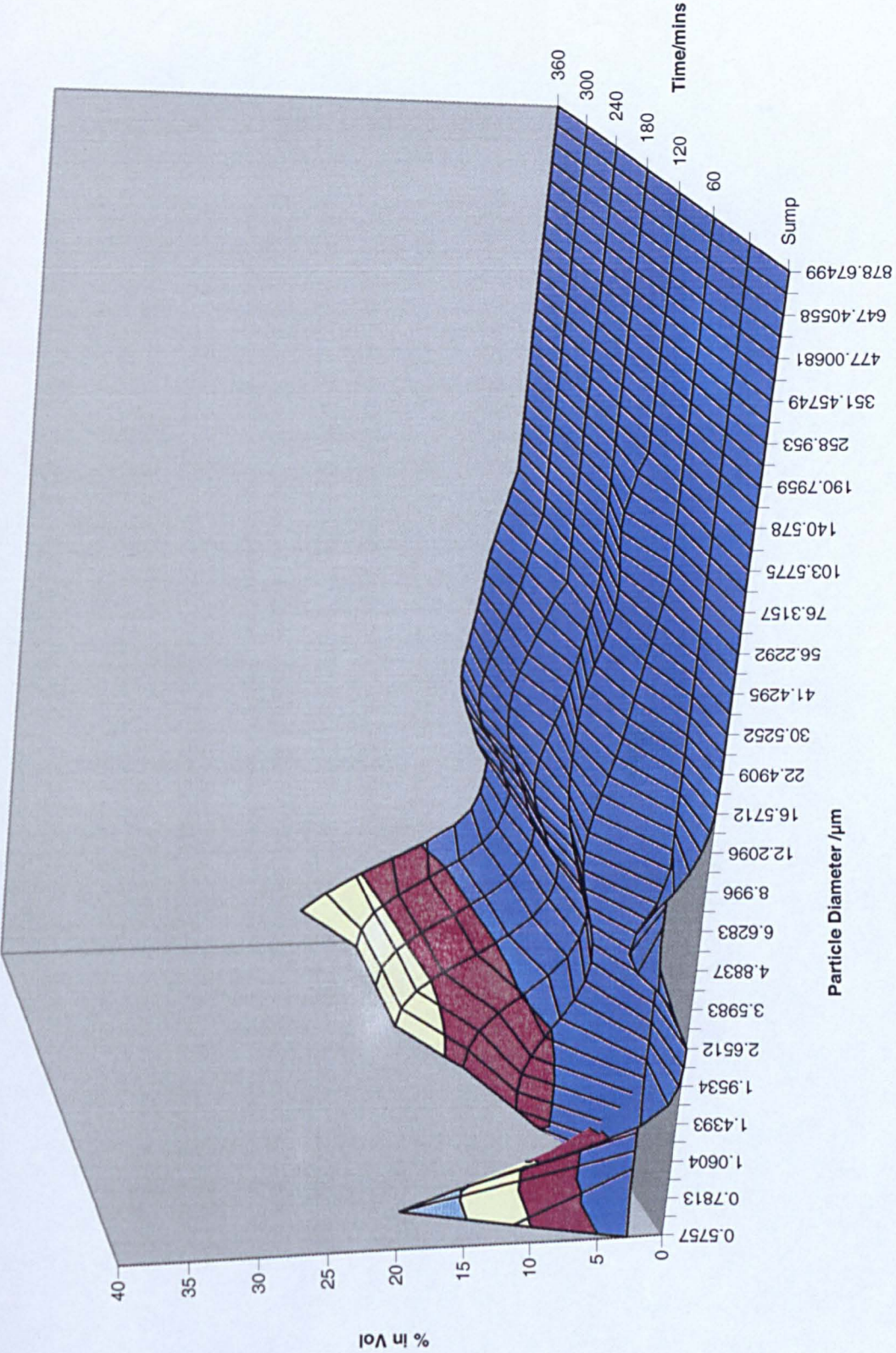
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/057c/02
W1 TRZ 60-360mins



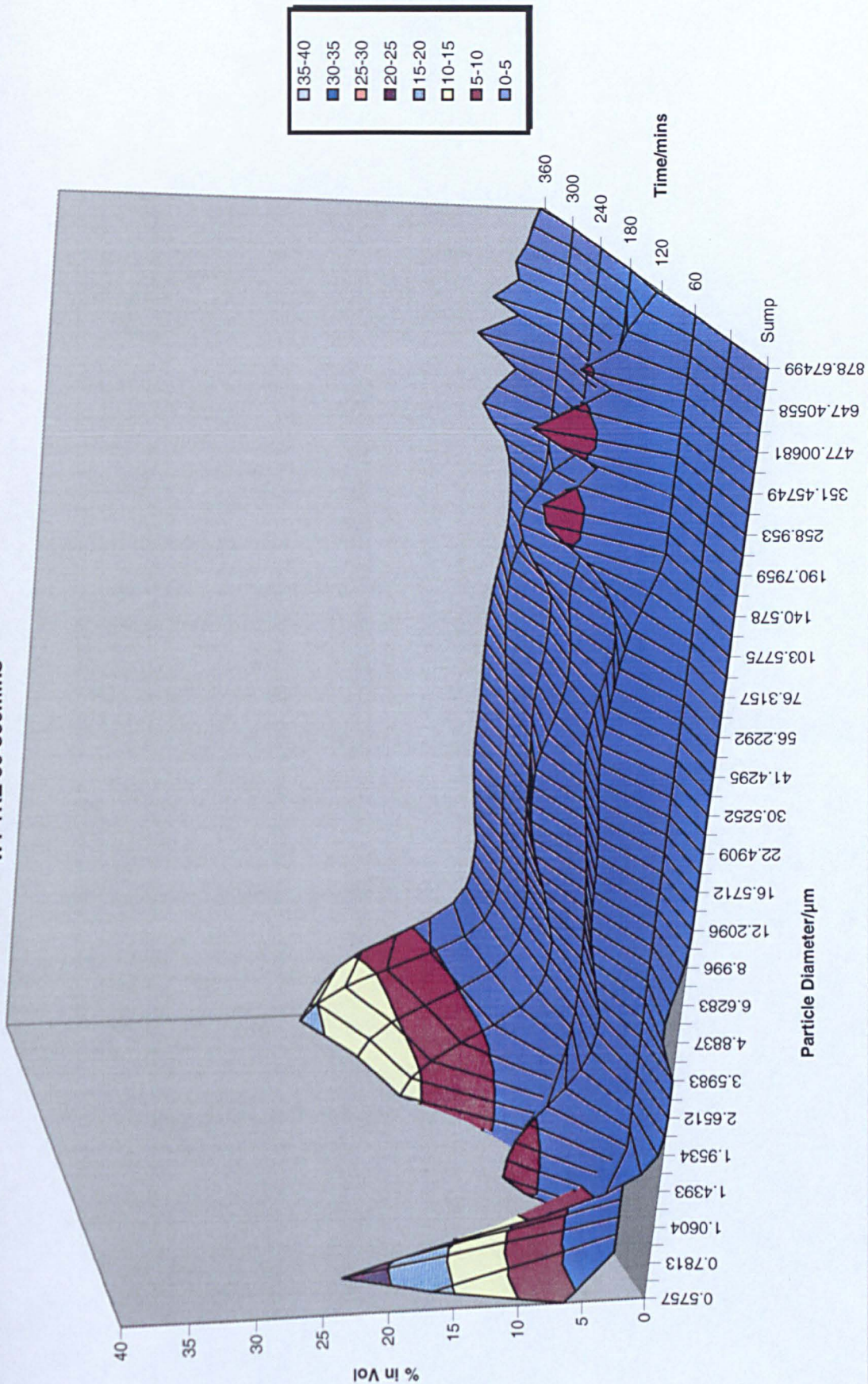
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058a/01
W1 TRZ 60-360mins



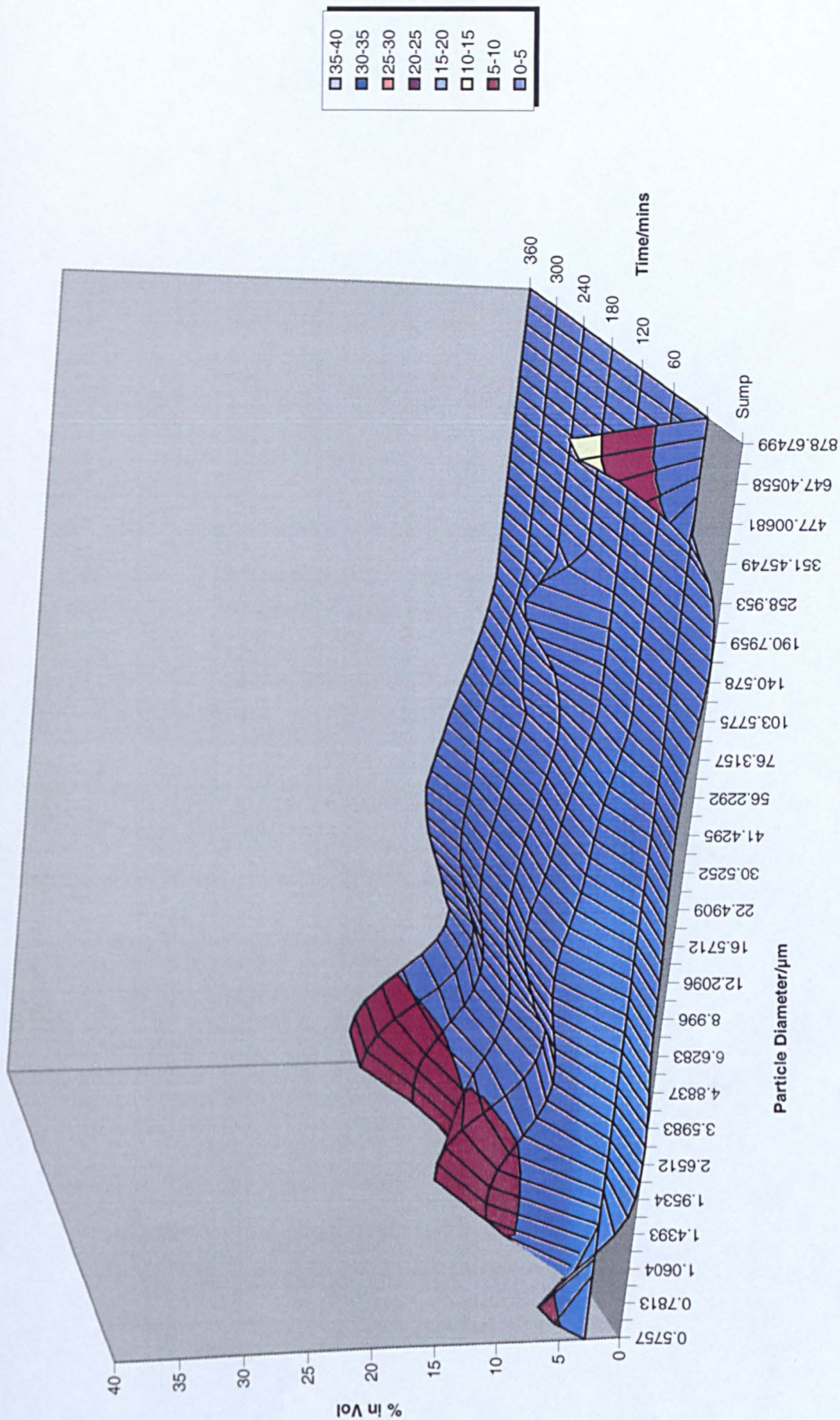
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058b/01
W1 TRZ 60-360mins



Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058c/01
W1 TRZ 60-360mins

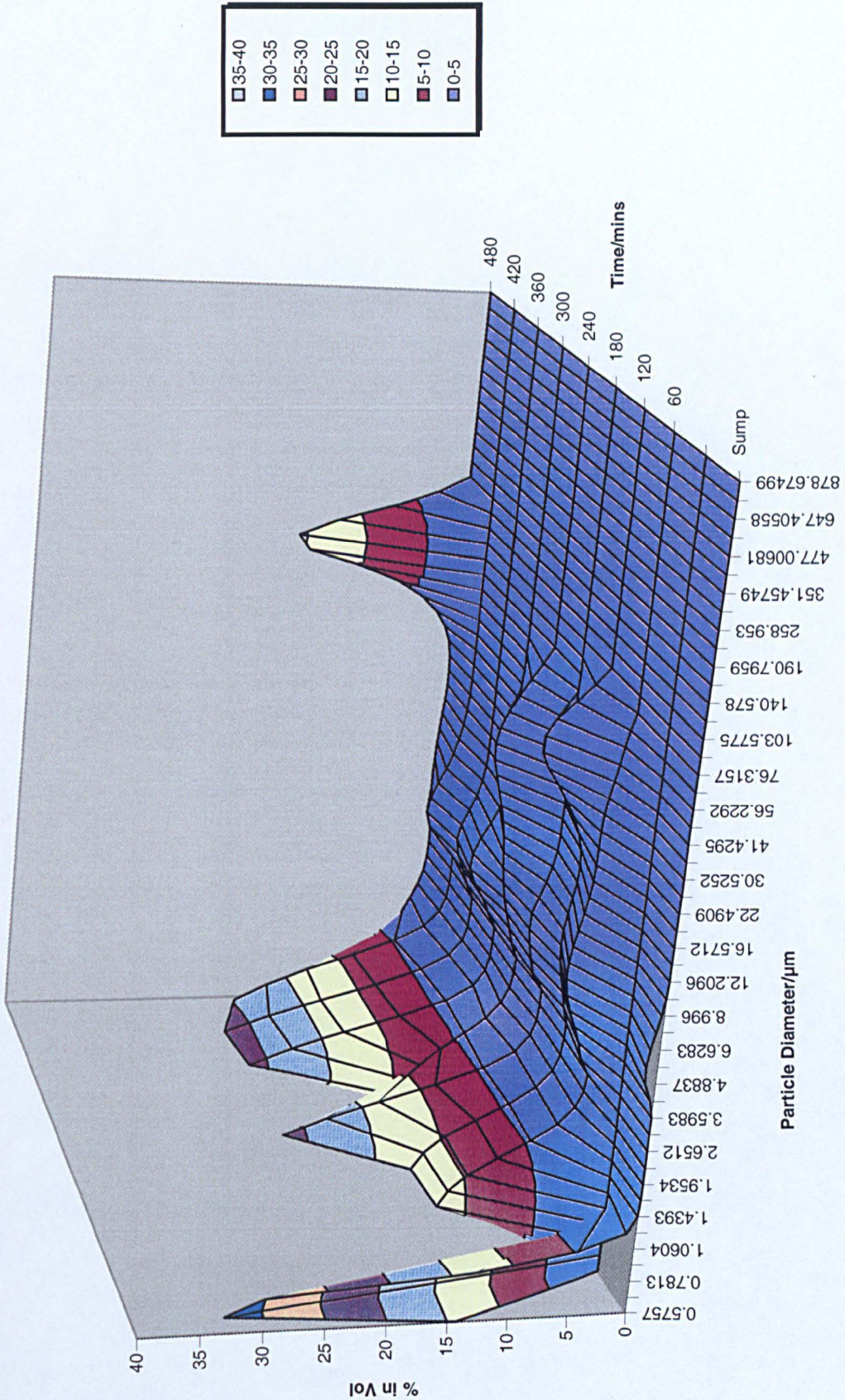


Elevation 15
Rotation 20
Perspective 30

6 of

Appendix 2 – Particle Size Contour Plots for Petter AA1

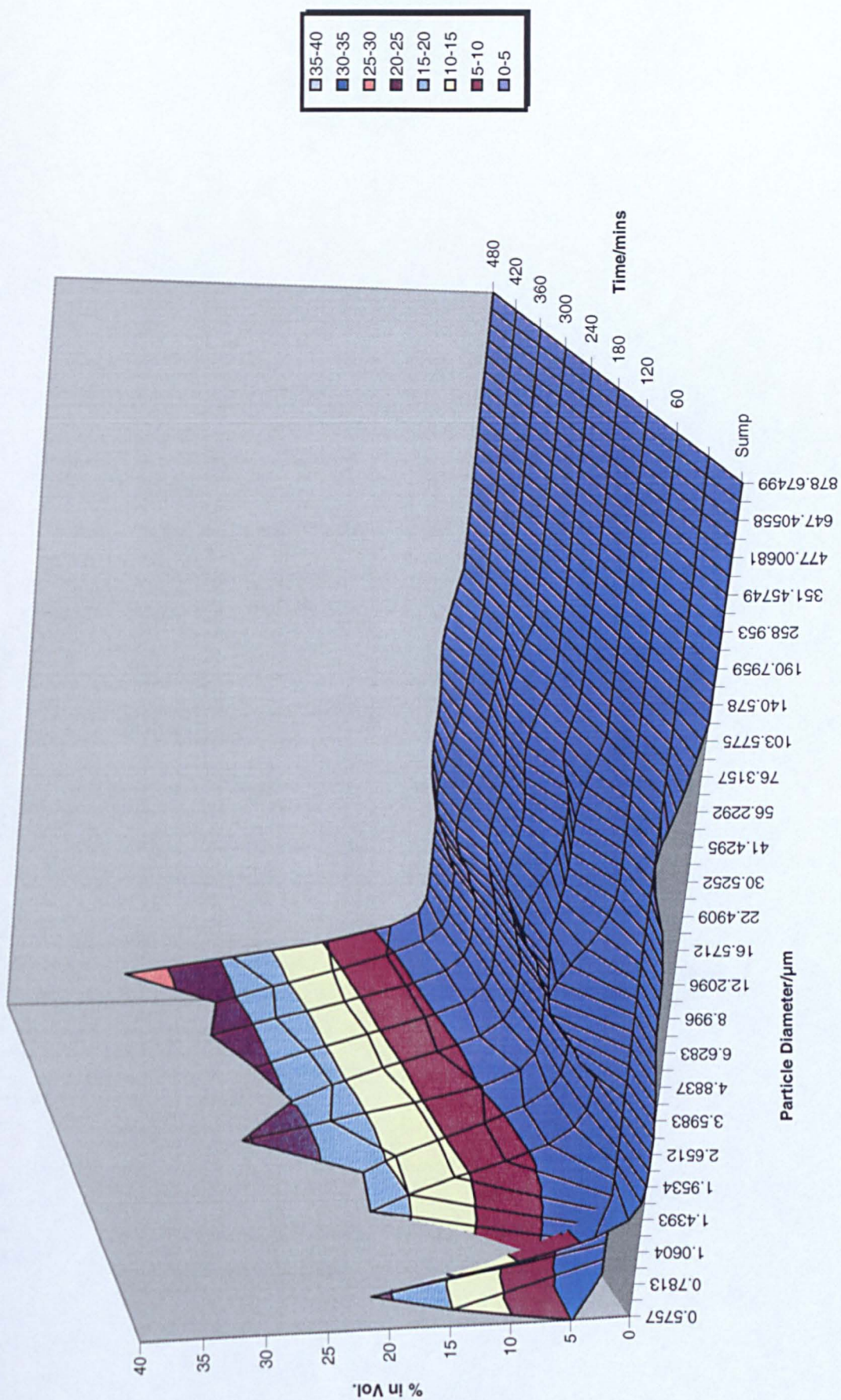
Particle Size Distribution for ATL953/057a/01
AA1 TRZ 60-480mins



Elevation 15
Rotation 20
Perspective 30

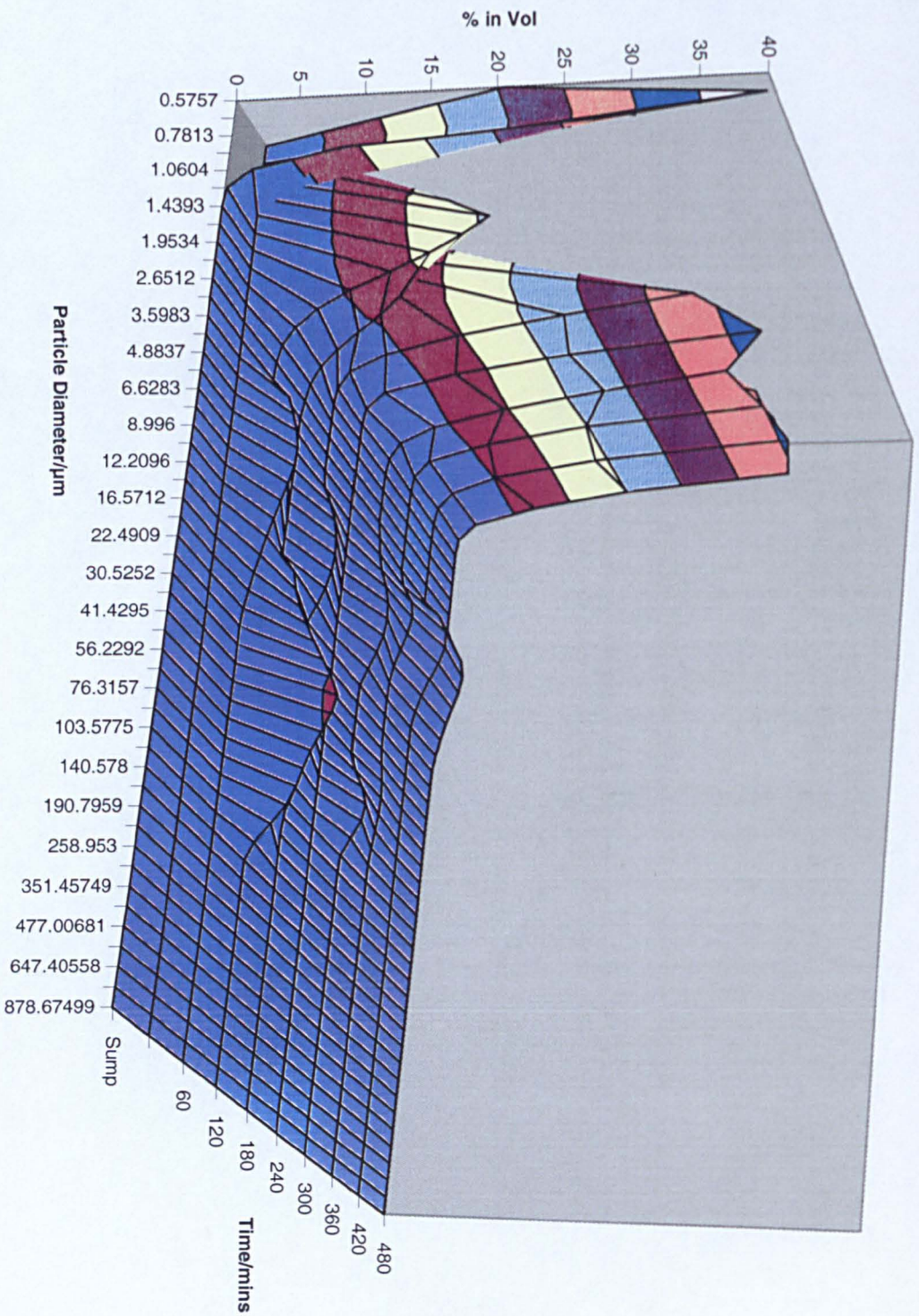
1 of 12

Particle Size Distribution for ATL953/057b/02
AA1 TRZ 60-480mins



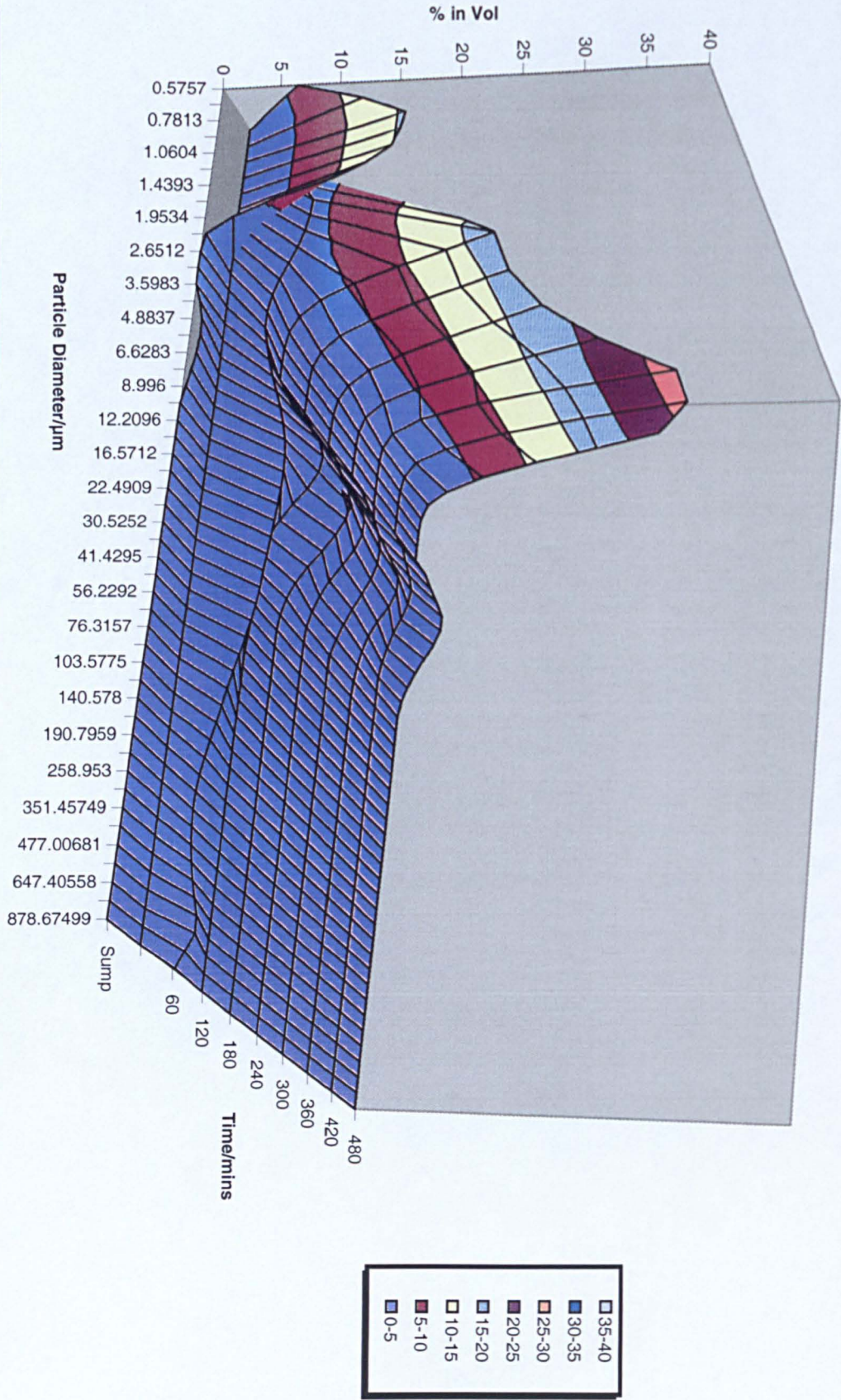
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/057c/02
AA1 TRZ 60-480mins



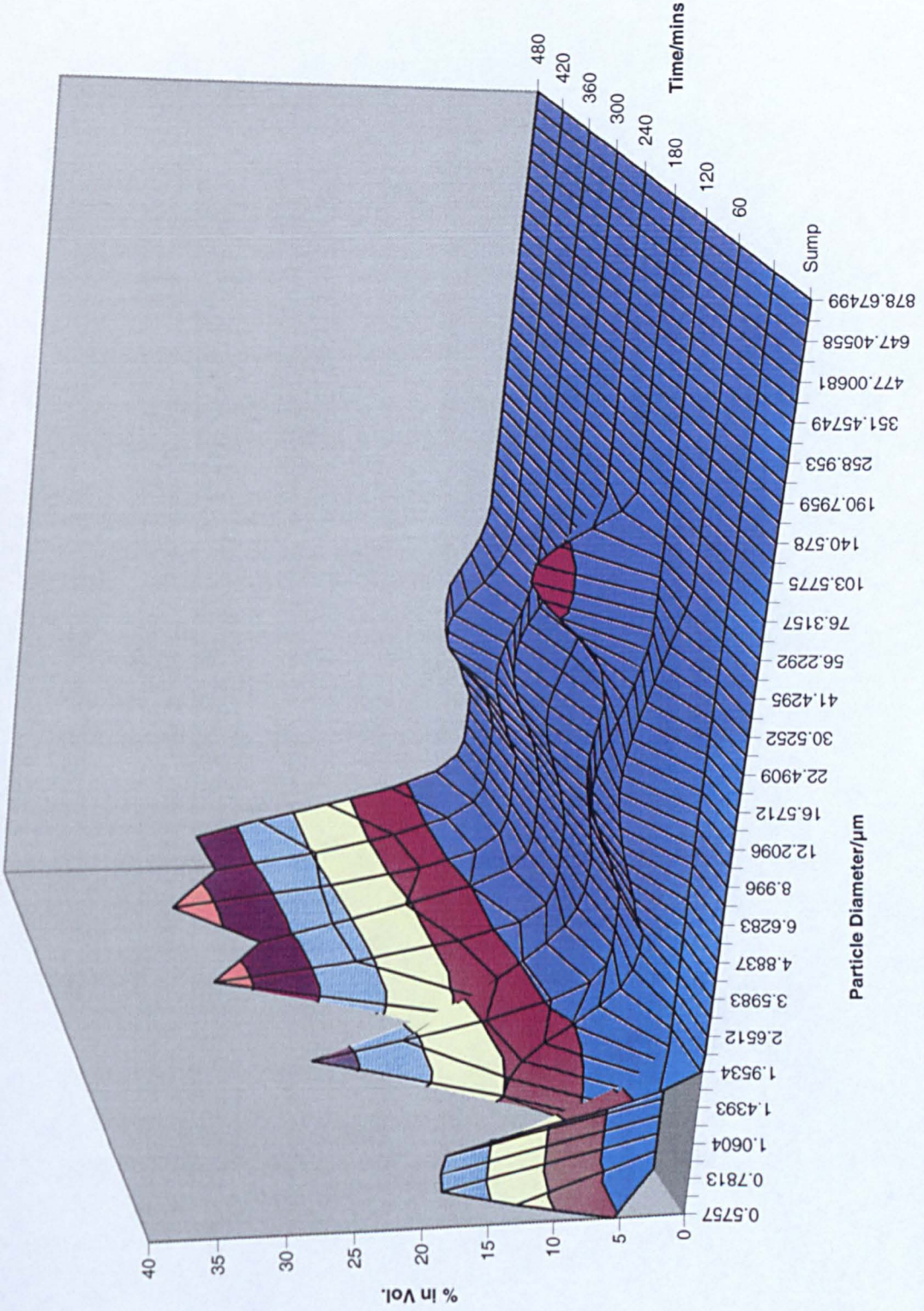
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/057d/01
AA1 TRZ 60-480mins



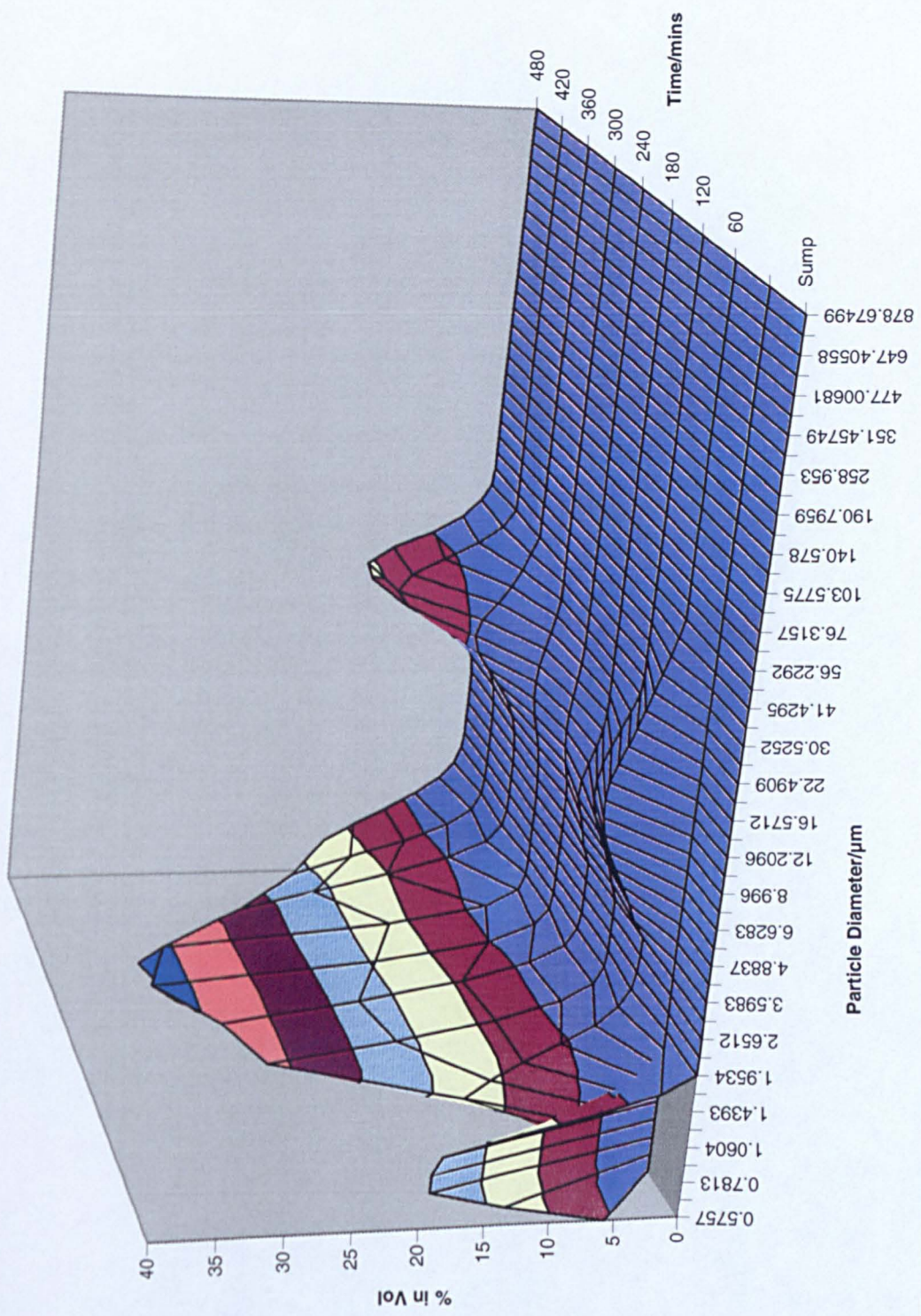
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/057e/01
AA1 TRZ 60-480mins



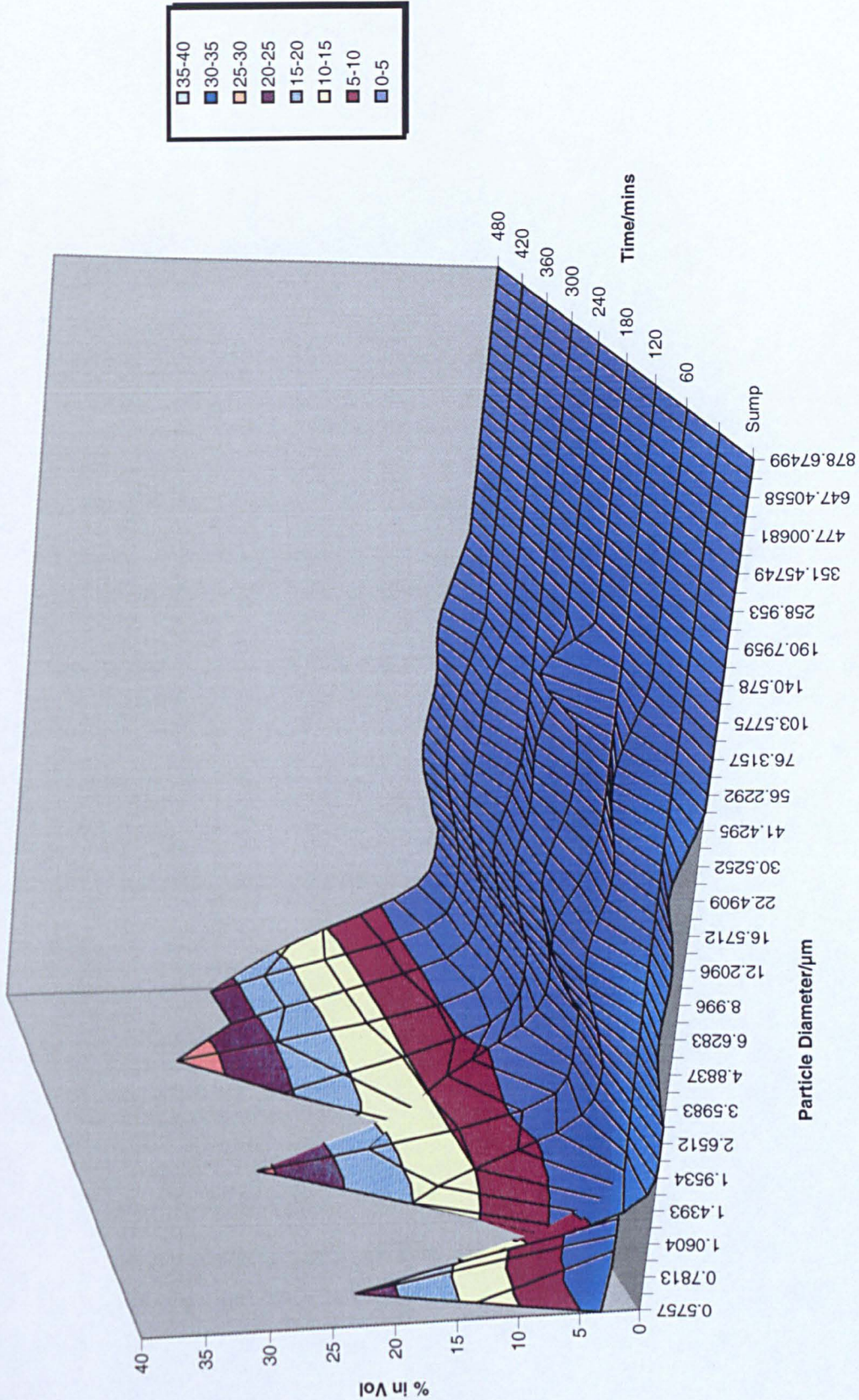
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/057f/01
AA1 TRZ 60-480mins



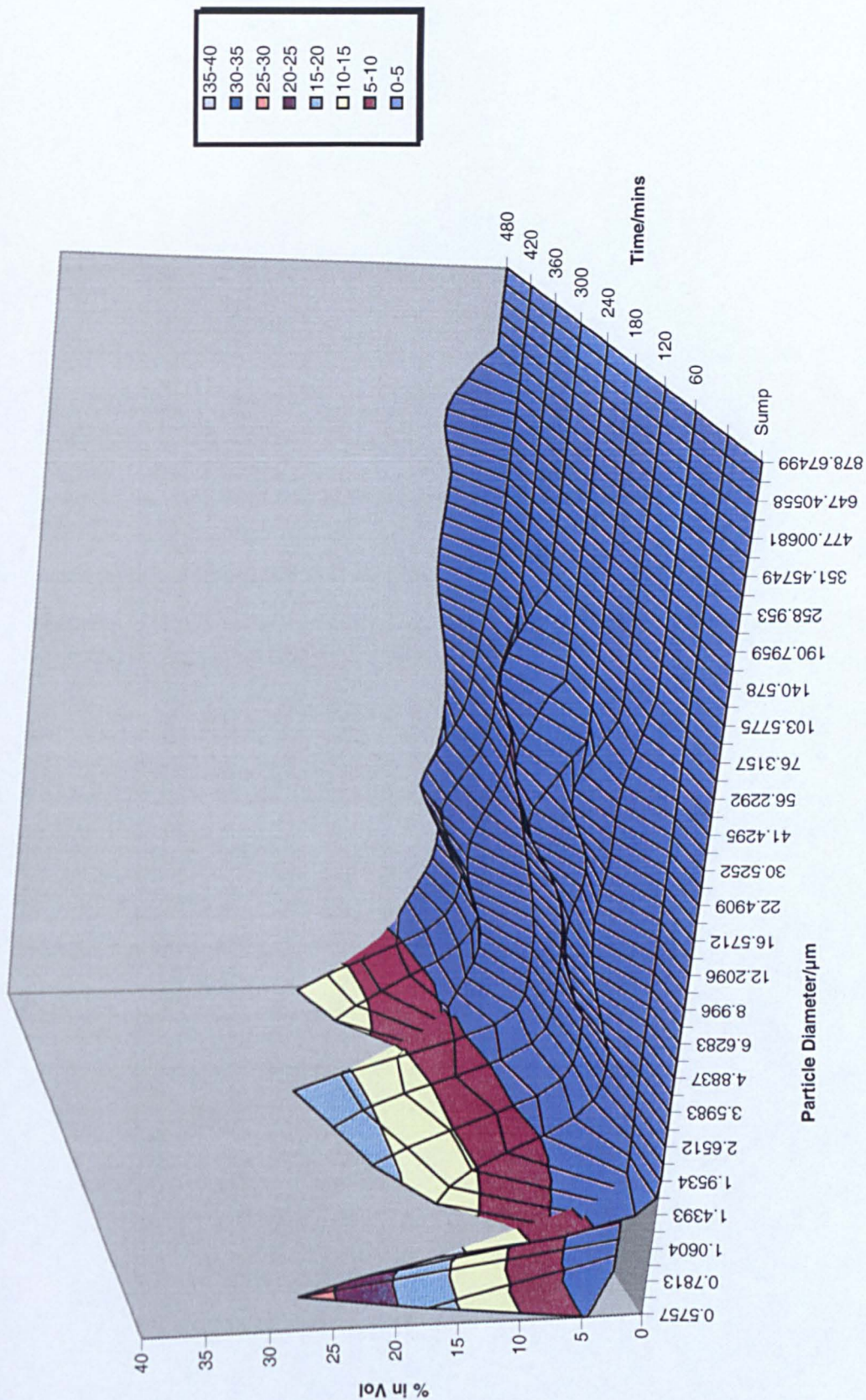
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058a/01
AA1 TRZ 60-480mins



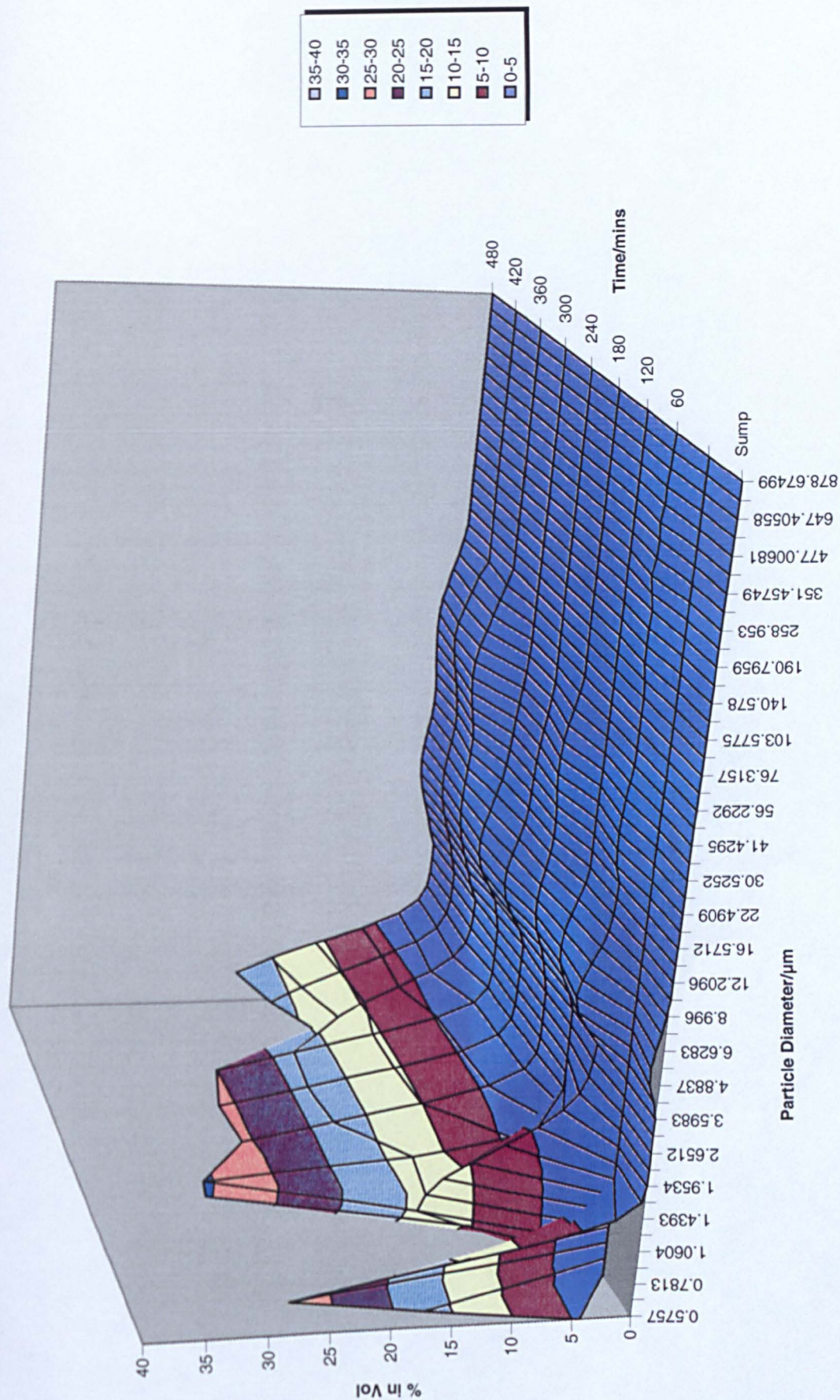
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058b/01
AA1 TRZ 60-480mins



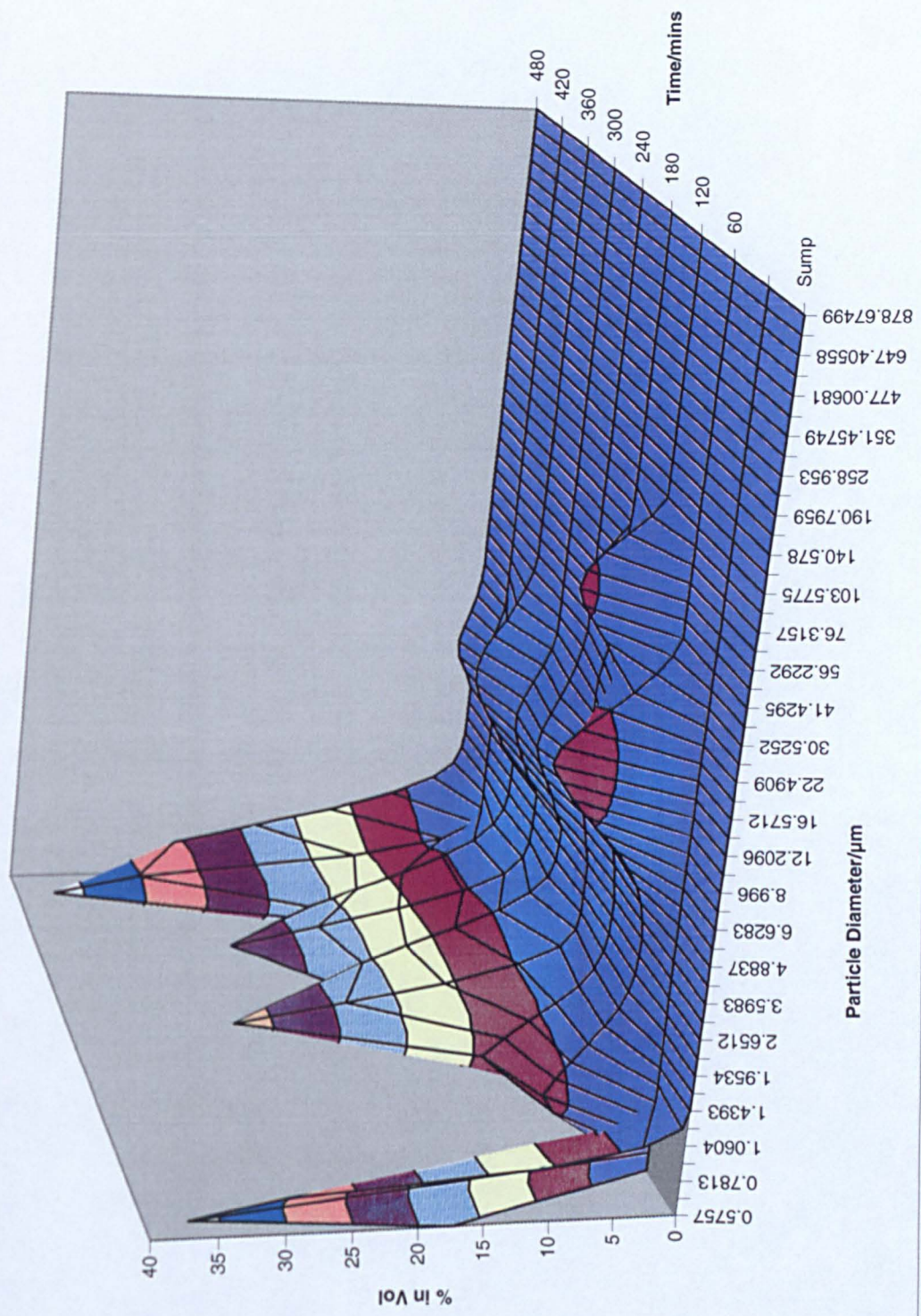
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058c/01
AA1 TRZ 60-480mins



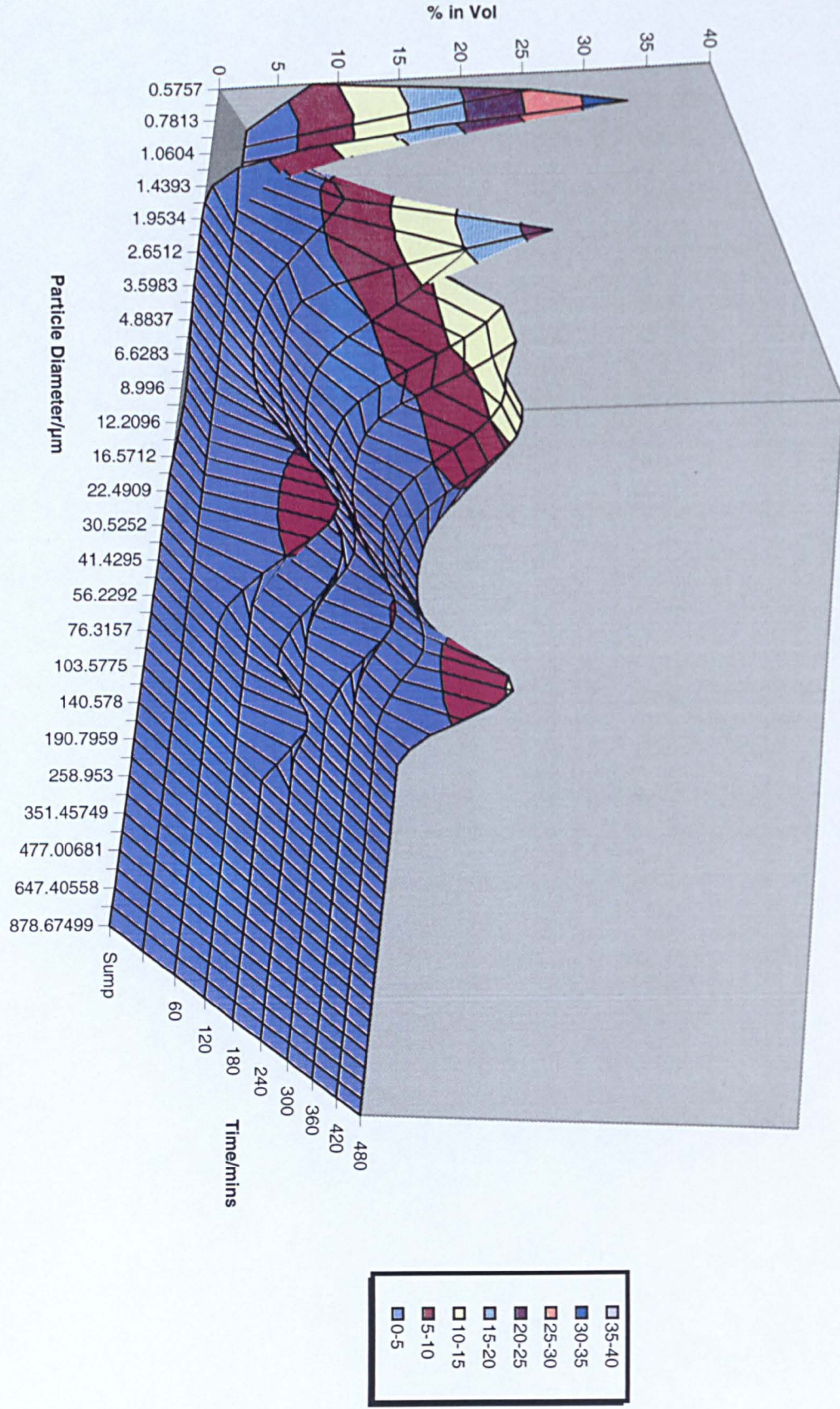
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058d/01
AA1 TRZ 60-480mins



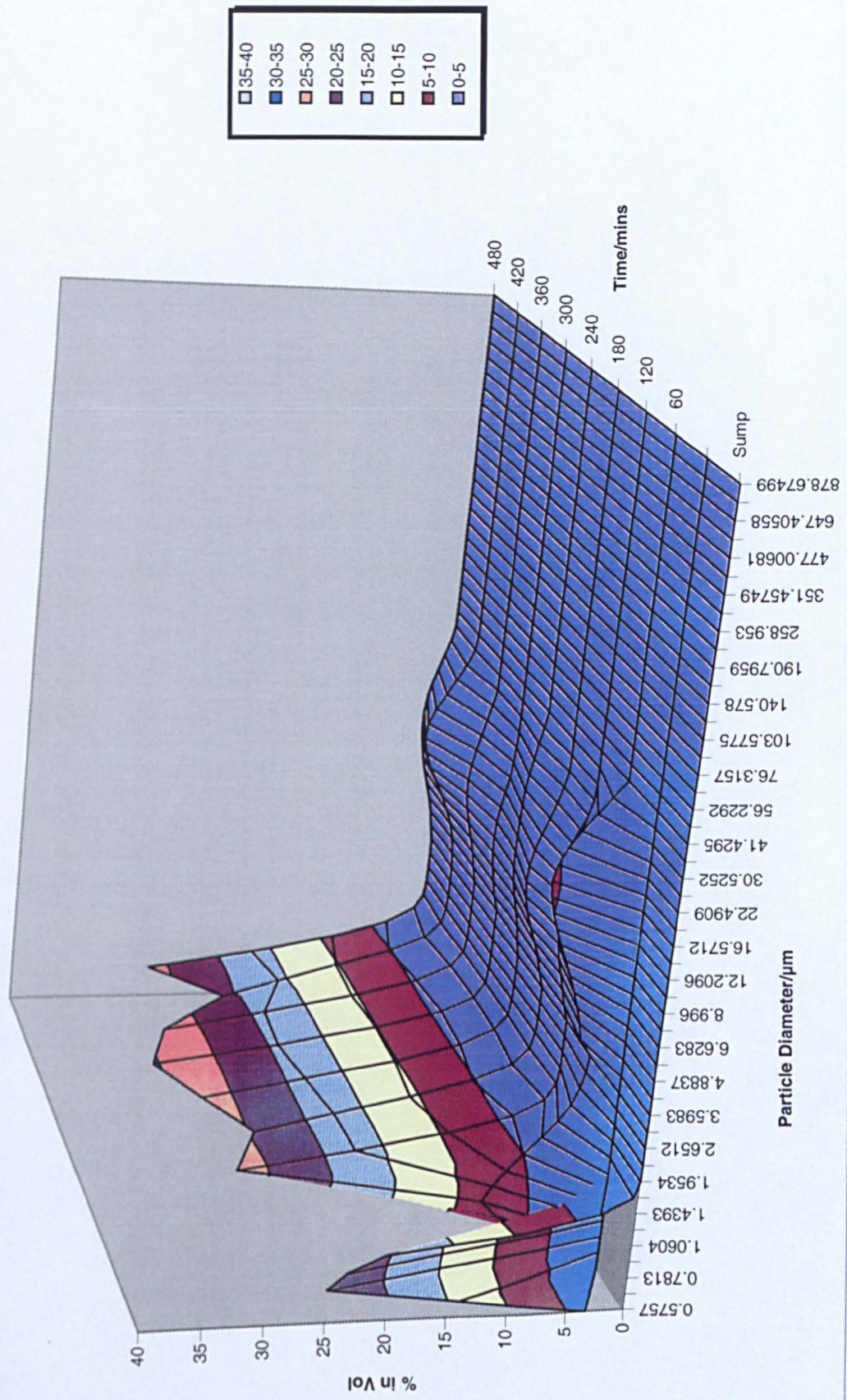
Elevation 15
Rotation 20
Perspective 30

Particle Size Distribution for ATL953/058e/01
AA1 TRZ 60-480mins



Elevation 15
Rotation 20
Perspective 30

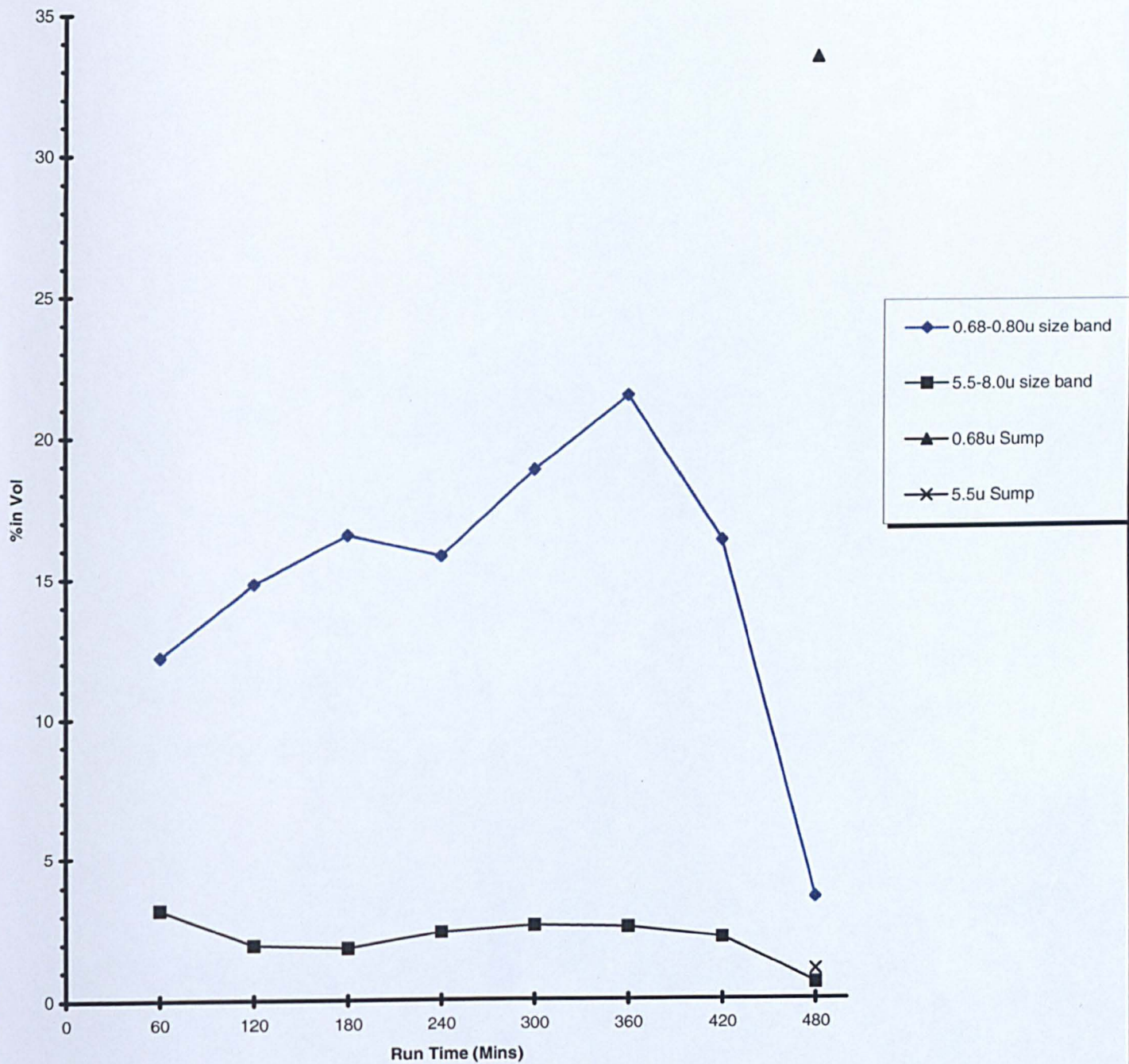
Particle Size Distribution for ATL953/058f/01
AA1 TRZ 60-480mins



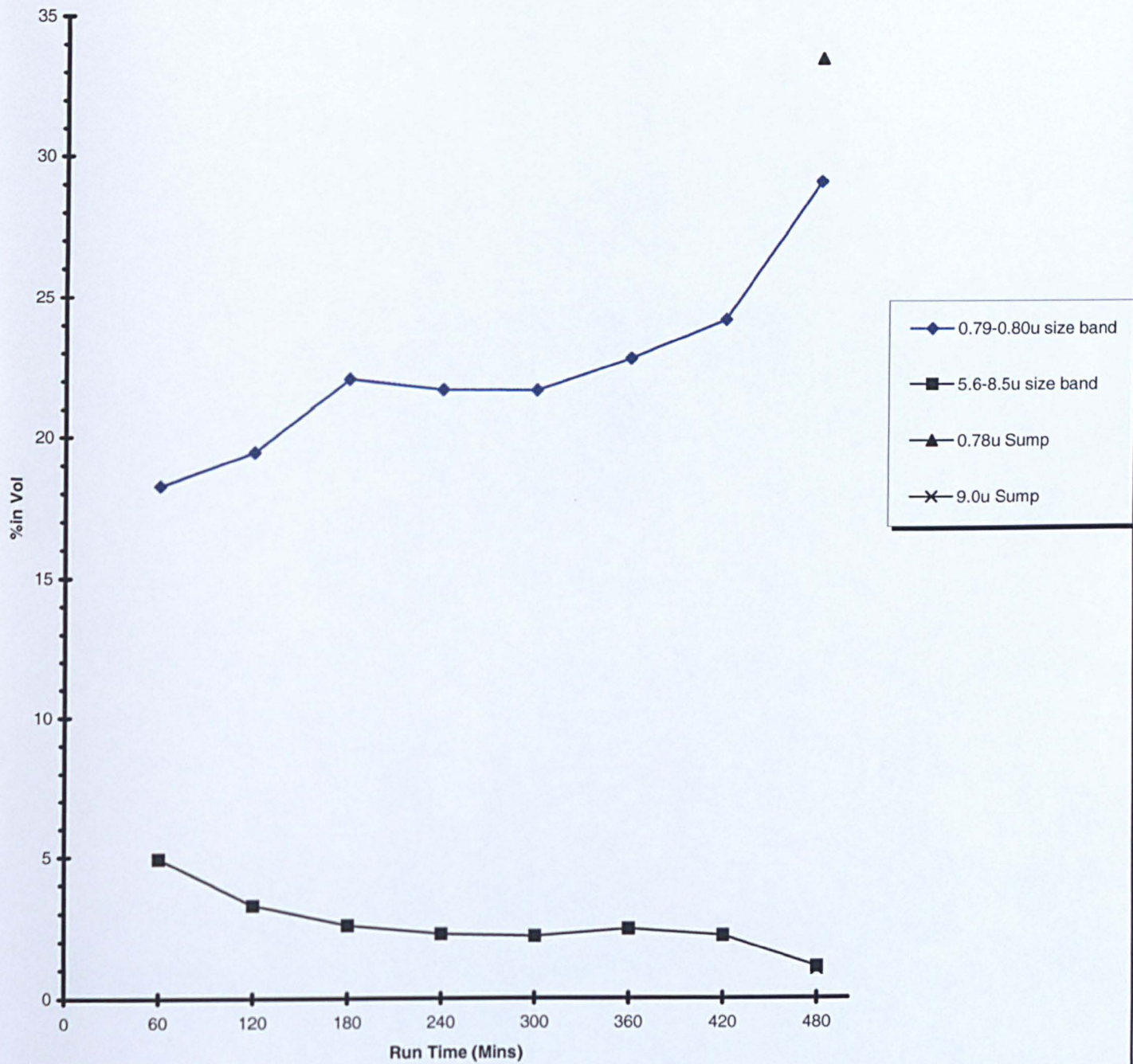
Elevation 15
Rotation 20
Perspective 30

Appendix 3 – First Sample Matrix Combined Results

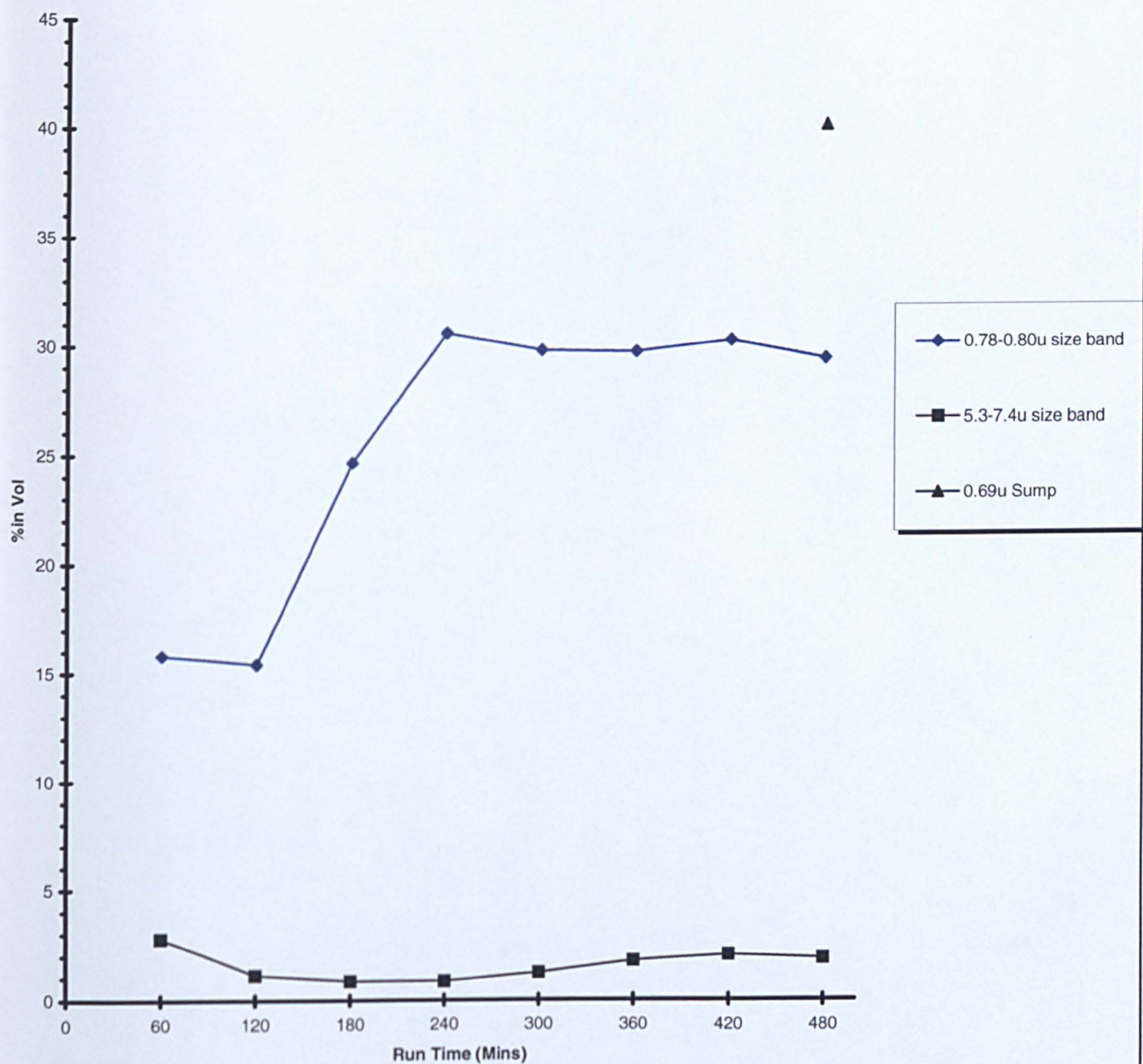
Changes in the Height of Size Bands vs Time
for 57A



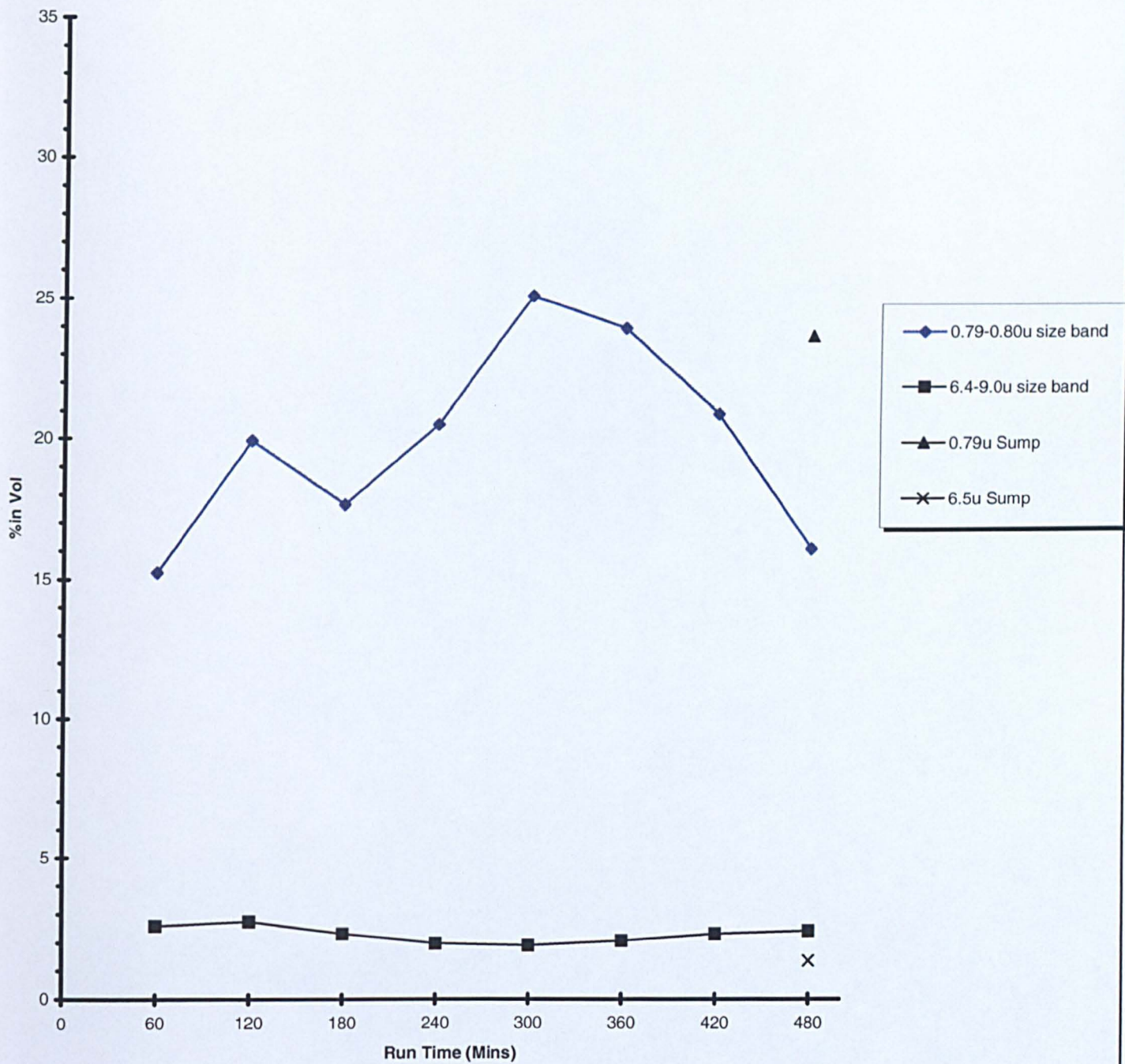
Changes in the Height of Size Bands vs Time
for 57B



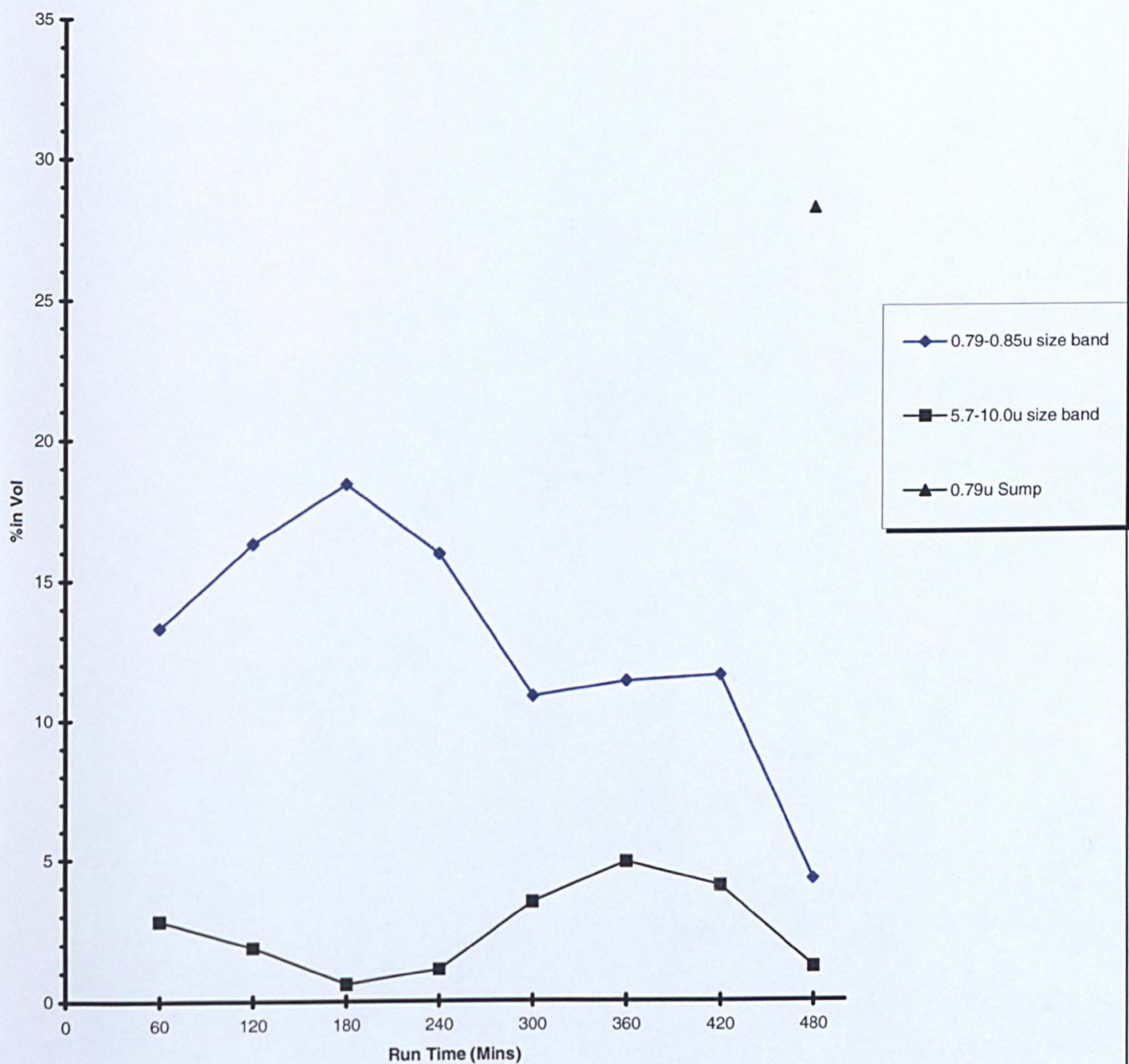
Changes in the Height of Size Bands vs Time
for 57C



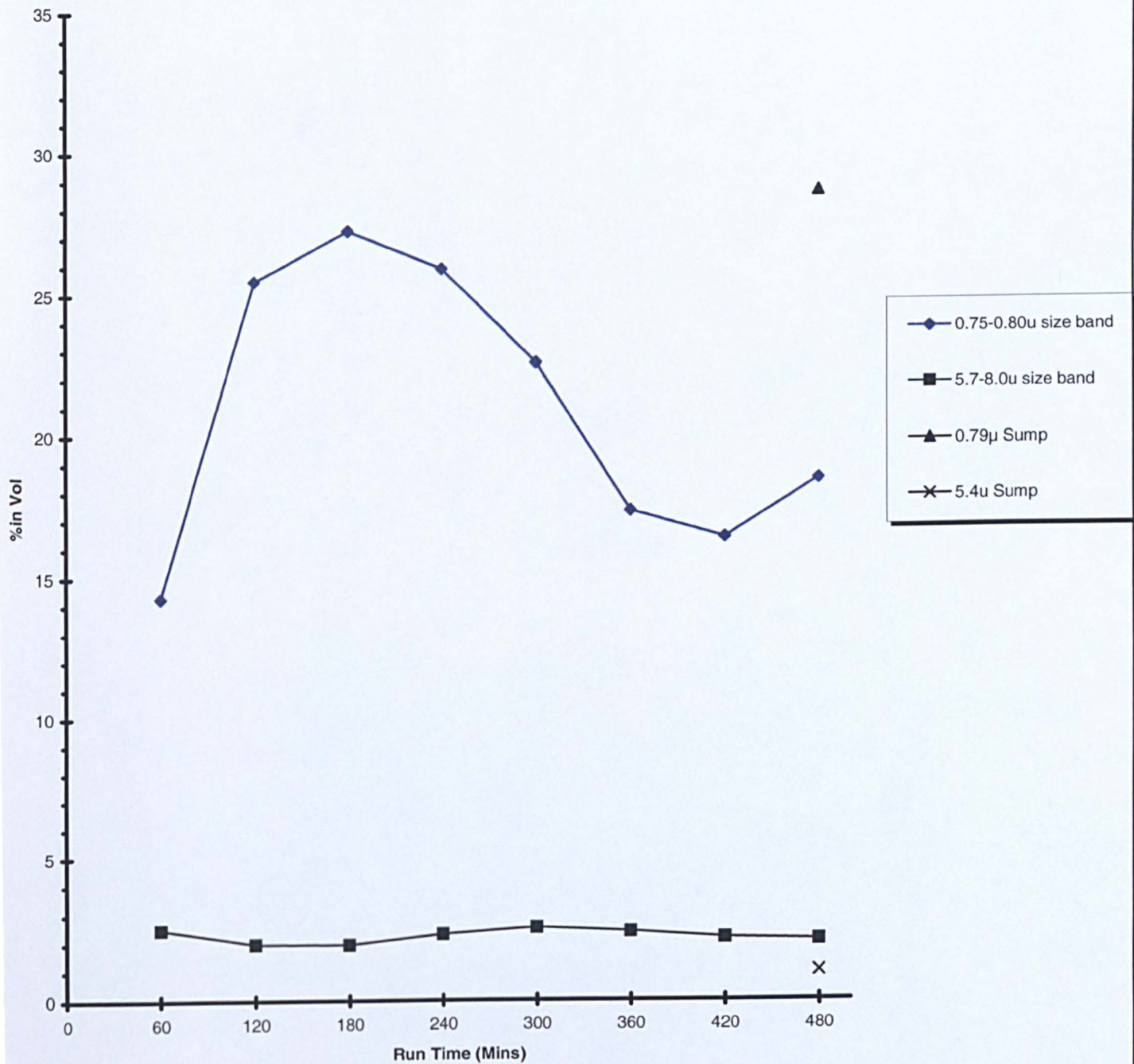
Changes in the Height of Size Bands vs Time
for 58A



Changes in the Height of Size Bands vs Time
for 58B

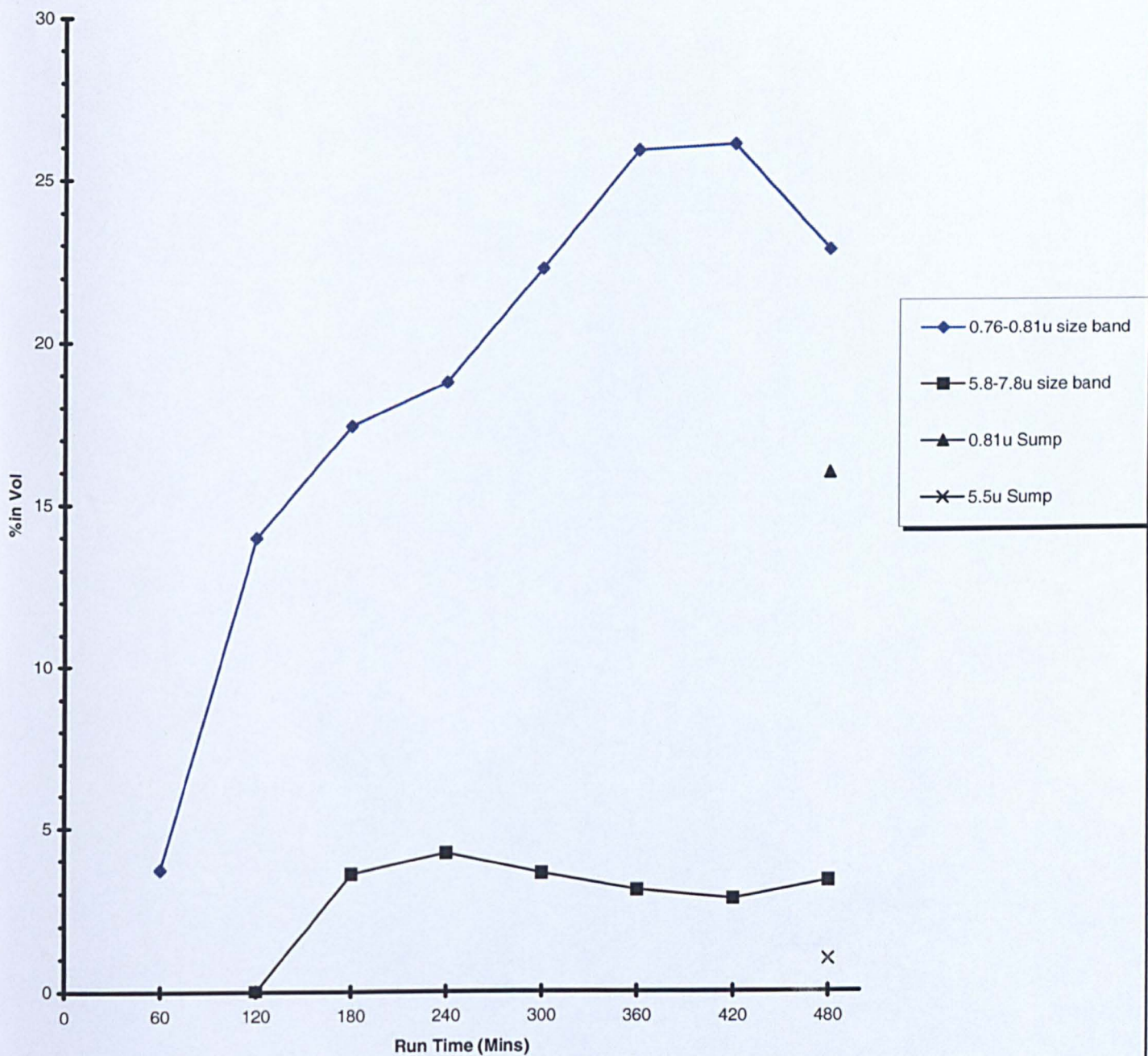


Changes in the Height of Size Bands vs Time
for 58C

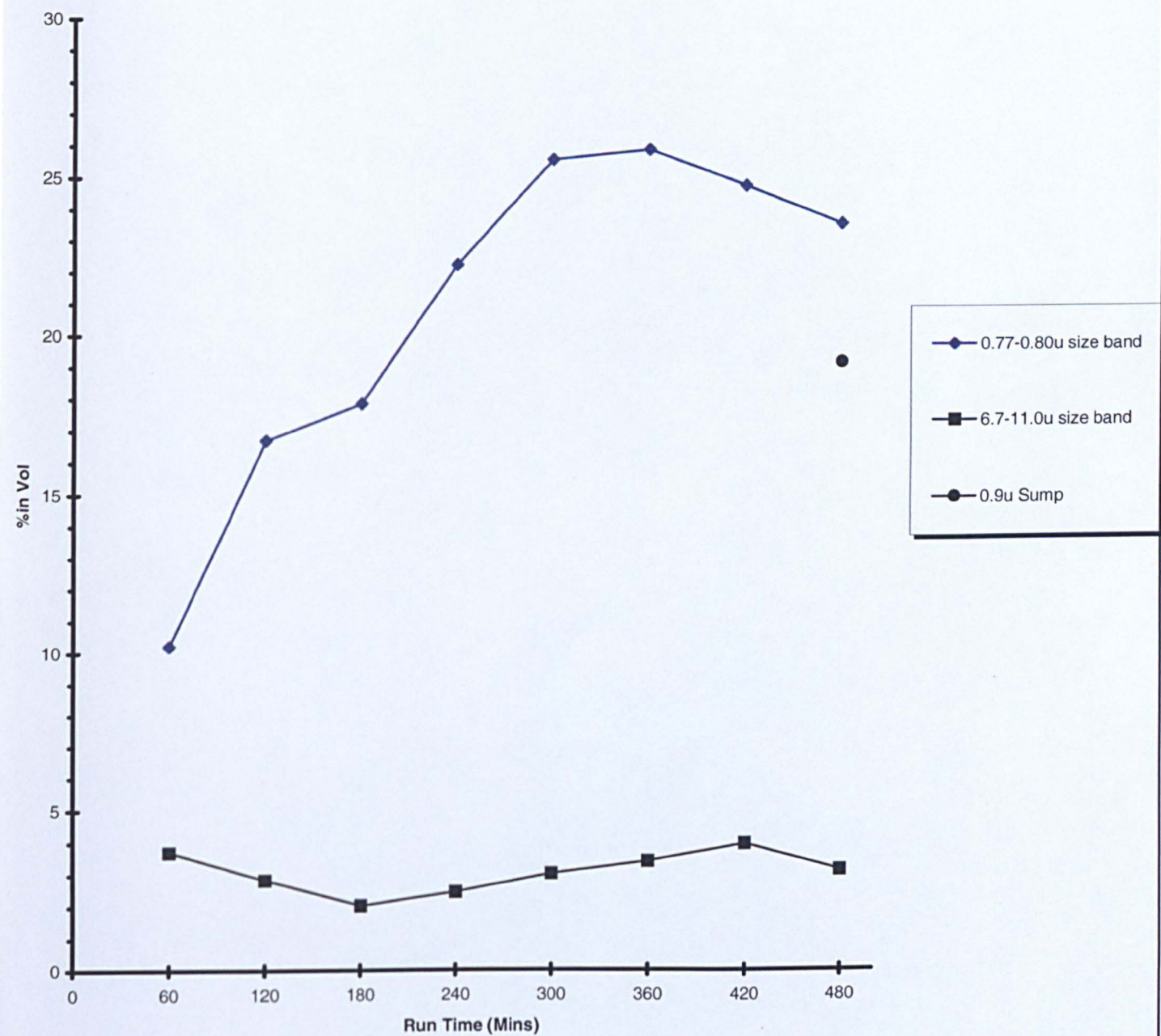


Appendix 4 – Second Sample Matrix Combined Results

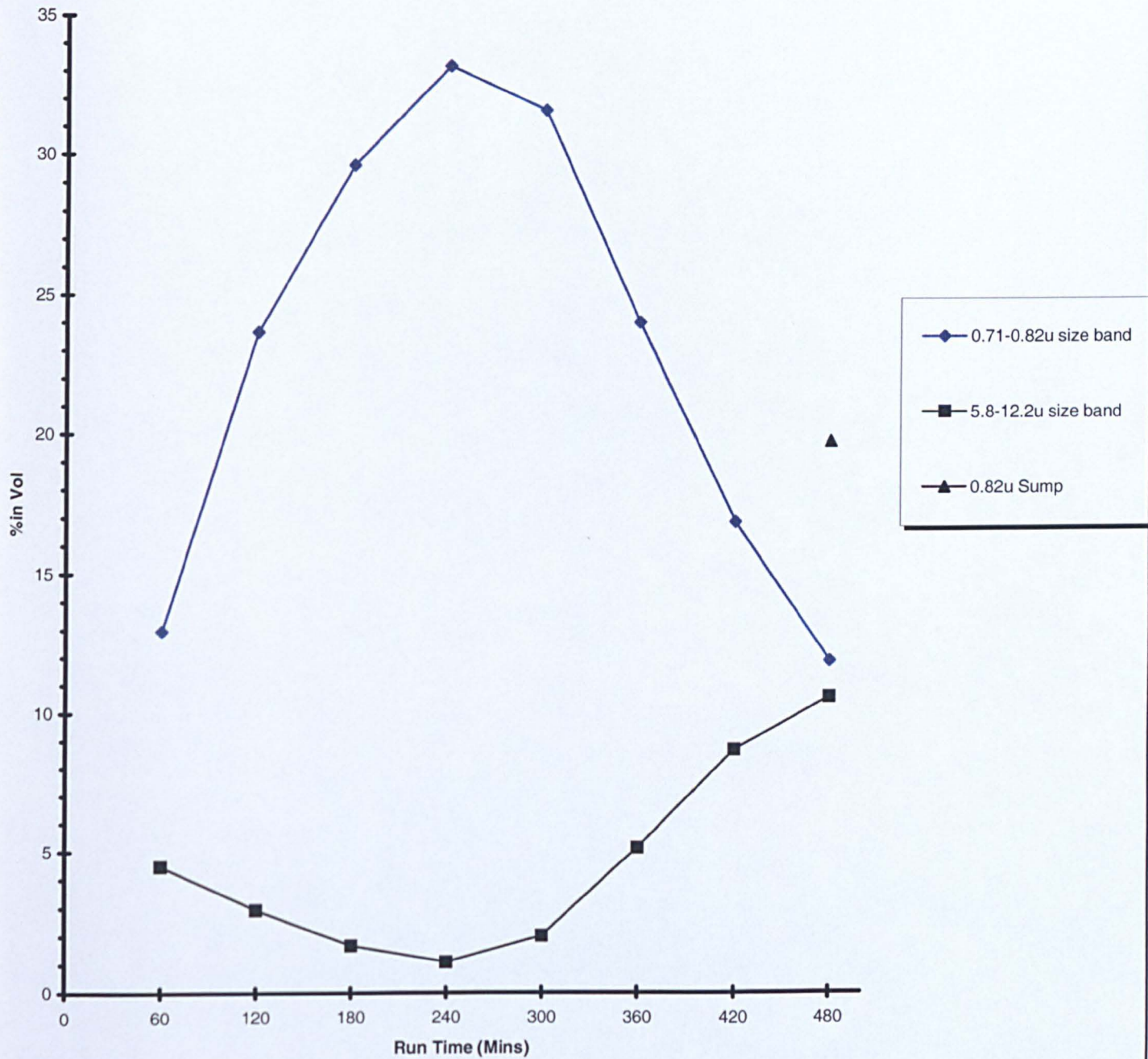
Changes in the Height of Size Bands vs Time
for 57D



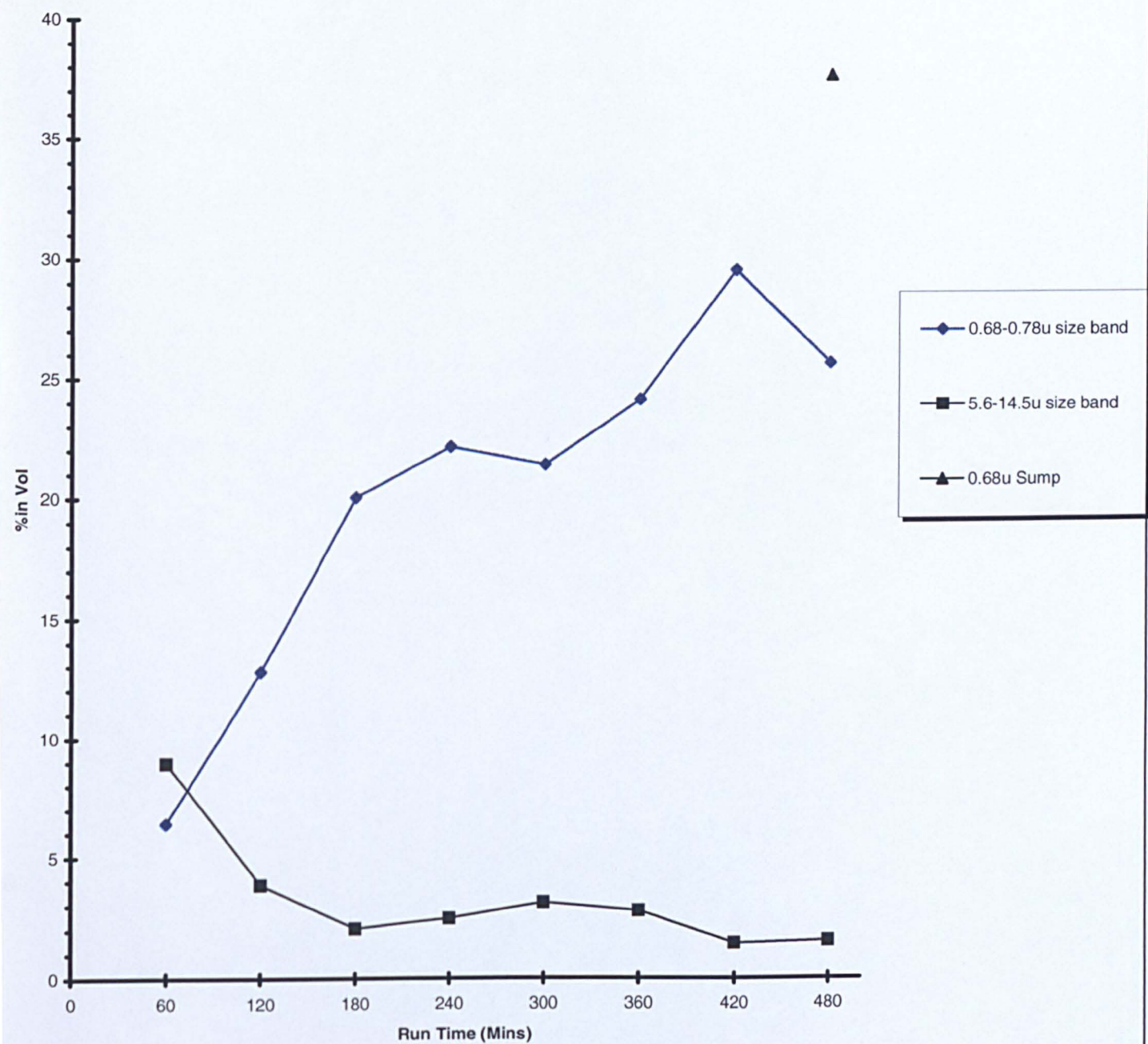
Changes in the Height of Size Bands vs Time
for 57E



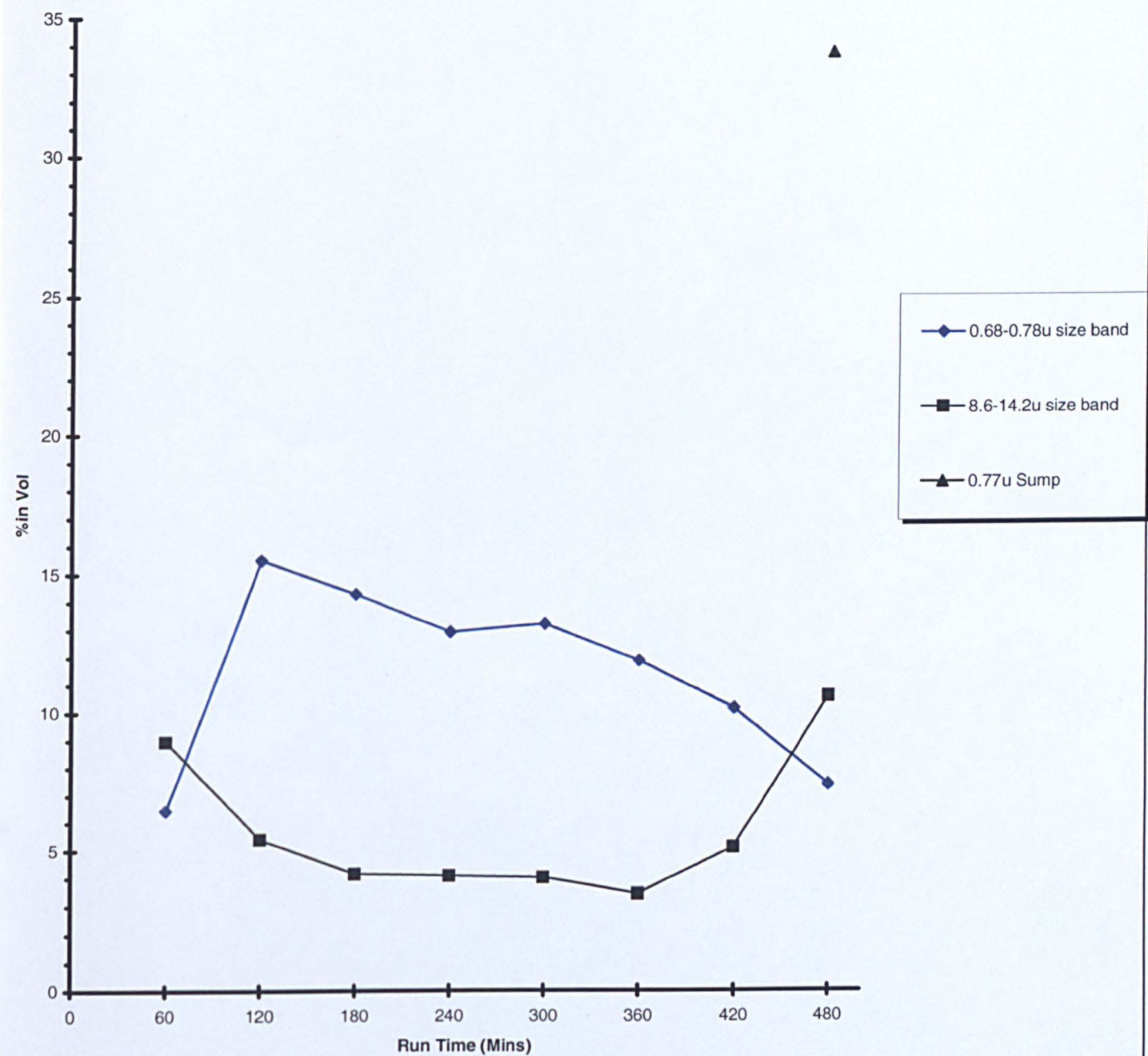
Changes in the Height of Size Bands vs Time
for 57F



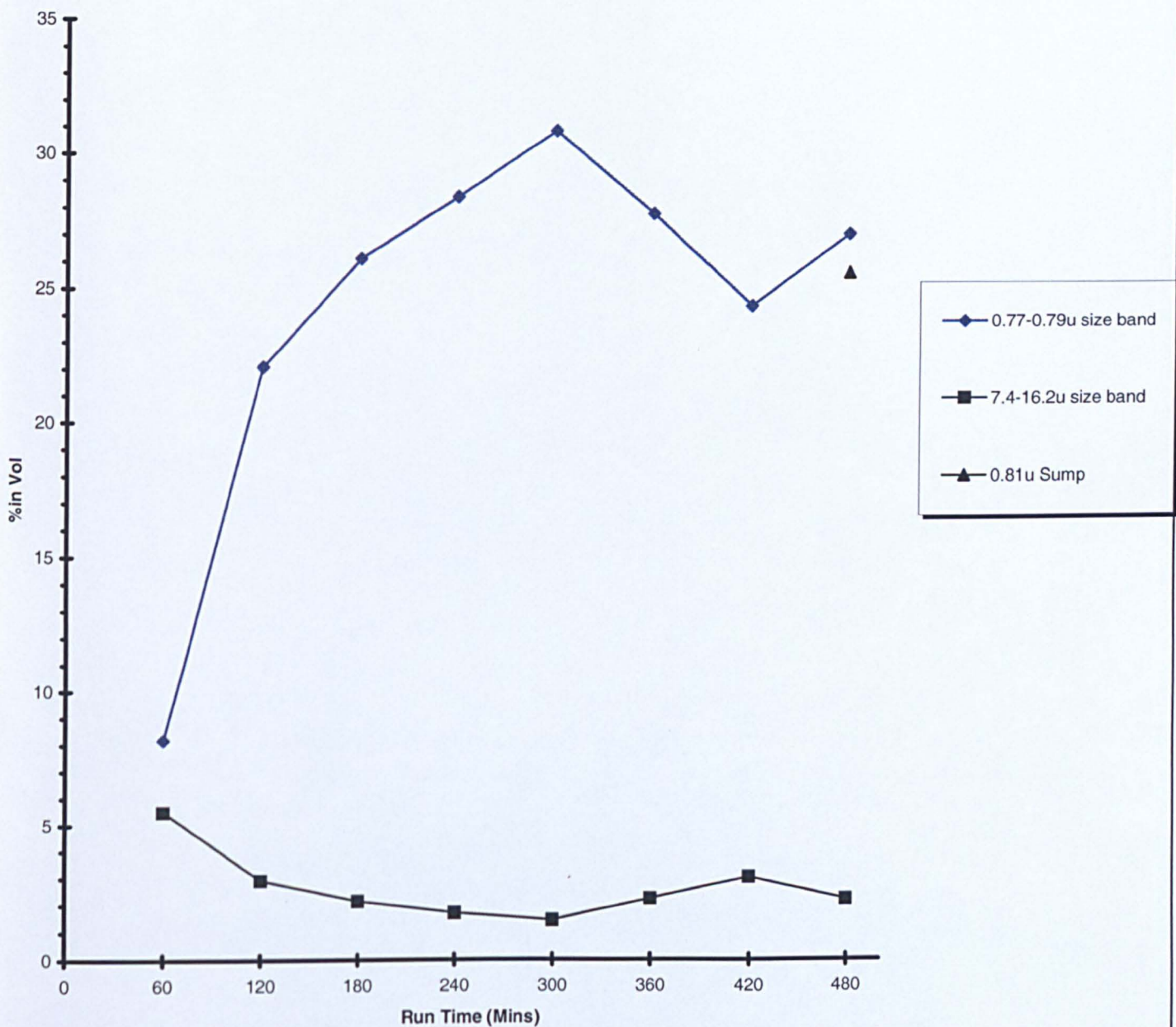
Changes in the Height of Size Bands vs Time
for 58D



Changes in the Height of Size Bands vs Time
for 58E



Changes in the Height of Size Bands vs Time
for 58F



Appendix 5 – Thermogravimetric Analysis Results

57D TGA Soot Values

Sump = 0.469%

TRZ 60min = 0.401%

TRZ 120min = 0.572%

TRZ 180min = 0.462%

TRZ 240min = 0.544%

TRZ 300min = 0.505%

TRZ 360min = 0.412%

TRZ 420min = 0.472%

TRZ 480min = 0.450%

AV (120-480) = 0.49%

57E TGA Soot Values

Sump = 0.337%

TRZ 60min = 0.647%

TRZ 120min = 0.497%

TRZ 180min = 0.488%

TRZ 240min = 0.426%

TRZ 300min = 0.600%

TRZ 360min = 0.599%

TRZ 420min = 0.509%

TRZ 480min = 0.599%

AV (120-480) = 0.53%

57F TGA Soot Values

Sump = 0.918%

TRZ 60min = 0.170%

TRZ 120min = 0.456%

TRZ 180min = 0.630%

TRZ 240min = 0.604%

TRZ 300min = 0.811%

TRZ 360min = 0.445%

TRZ 420min = 0.909%

TRZ 480min = 0.691%

AV (120-480) = 0.65%

58D TGA Soot Values

Sump = 0.706%

TRZ 60min = 0.669%

TRZ 120min = 0.821%

TRZ 180min = 0.316%

TRZ 240min = 0.727%

TRZ 300min = 0.802%

TRZ 360min = 0.882%

TRZ 420min = 0.952%

TRZ 480min = 0.867%

AV (120-480) = 0.77%

58E TGA Soot Values

Sump = 0.694%

TRZ 60min = 0.696%

TRZ 120min = 0.533%

TRZ 180min = 0.660%

TRZ 240min = 0.672%

TRZ 300min = 0.569%

TRZ 360min = 0.533%

TRZ 420min = 0.736%

TRZ 480min = 0.500%

AV (120-480) = 0.70%

58F TGA Soot Values

Sump = 0.482%

TRZ 60min = 0.639%

TRZ 120min = 0.784%

TRZ 180min = 0.589%

TRZ 240min = 0.471%

TRZ 300min = 0.438%

TRZ 360min = 0.607%

TRZ 420min = 0.440%

TRZ 480min = 0.278%

AV (120-480) = 0.52%